SPECTROSCOPIC STUDIES ON THE NATURE OF THE METAL - HALOGEN BOND

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ABSTRACT

The work described in this thesis is concerned with the study by spectroscopic methods of the metal - halogen bond in complexes of a variety of metal ions in various stereochemistries and oxidation states. The complexes chosen for study contained, in addition to the halogeno-ligands Cl, Br and I, tertiary phosphines, and hence spectroscopic studies of the metal - phosphorus bond have also been possible.

The spectroscopic techniques used were those of low frequency infra-red; ^{1}H, ^{13}C and ^{31}P NMR; and electronic absorption spectroscopy.

Three distinct but related systems have been investigated.

1) Four - coordinate complexes of nickel (II), palladium (II) and platinum (II) (all square planar), and of cobalt (II) and zinc (II) (both tetrahedral), of form MX_2L_2 (where X = Cl, Br, I ; L = PEt_3 and Et_2PhP), and binuclear halogen-bridged species of form $M_2X_4L_2$ (M = Pd, Pt; L = PEt_3 ; X is as above) have been prepared and studied. Attempts to prepare four-coordinate rhodium (I) complexes of triethylphosphine and diethylphenylphosphine are also described. The complexes have been studied by the spectroscopic techniques outlined above and the results related, where possible, to the nature of the metal - halogen bond. In particular, chemical shift trends with change in halogen for ^{1}H, ^{13}C and ^{31}P NMR spectra have been related to a component of $M_{d\pi} \longrightarrow X_{d\pi}$ metal - halogen π-bonding in the complexes. Other explanations for the observed deshielding trends, most notably the paramagnetic anisotropy of the diamagnetic

d^8 metal ion, have also been examined in the light of the constancy of resonances in the NMR spectra of zinc (II) complexes with change in halogen.

In the infra-red spectra of the complexes, revised assignments have been made for the metal - phosphorus stretching vibrations, and an intense absorption near 200 cm^{-1} has been assigned to the metal - phosphorus - carbon bending mode.

2) (a) Rhenium (V) halogeno - phosphine complexes containing oxo or nitrido ligands have been prepared and studied. These compounds have the form $ReOX_3L_2$ and $ReNX_2L_3$ (X = Cl,Br,I ; L = PEt_3, Et_2PhP). The stereochemistries of the oxo complexes have been elucidated from NMR spectra by an analysis of the different methyl resonance multiplicities for <u>cis</u> and <u>trans</u> phosphine ligands. In addition to the NMR studies, the low frequency infra-red and electronic spectra of the complexes have been recorded and principal absorptions assigned.

(b) Rhenium halogeno-phosphine complexes containing nitric oxide as a ligand have been prepared and studied by ^1H NMR, infra-red and electronic absorption spectroscopy. The complexes have the form $ReX_3(NO)L_2$ (X = Cl,Br,I ; L = Et_2PhP), with rhenium in the divalent oxidation state. This was suspected from magnetic moment measurements and confirmed from the communicated results of a single crystal X-ray structure determination of a related chloro complex. The electronic spectra can be interpreted in terms of divalent rhenium with the d^5 electron configuration. The $ReX_3(NO)L_2$ complexes can be reduced to the univalent rhenium complexes, $ReX_2(NO)L_3$, with

sulphite ion in the presence of excess of phosphine. Variations in the preparations of $ReX_3(NO)L_2$ complexes have been studied. Thus, bubbling nitric oxide through solutions of ReX_3L_3 complexes gives $ReX_3(NO)L_2$ species. In contrast, ReX_4L_2 compounds undergo no reaction with nitric oxide. Other preparative methods investigated were (i) thermal decomposition of Ag_2ReX_6 (X = Cl,Br) salts in a stream of nitric oxide and treatment of the residues with Et_2PhP to give the univalent rhenium complexes, $ReX_2(NO)(Et_2PhP)_3$ and, (ii), reaction of the anion $[ReX_5(NO)]^{2-}$ with Et_2PhP did not lead to identifiable products.

(c) The phosphine complex chemistry of technetium has been briefly investigated and shown to be analogous with that of rhenium.

3) Octahedral ruthenium (III) and ruthenium (II) complexes have been prepared and studied by ^1H, ^{13}C and ^{31}P NMR; low frequency infra-red, and electronic absorption spectroscopy. The complexes have the form RuX_3L_3 (X = Cl, Br; L = PEt_3, Et_2PhP) for ruthenium (III) and $RuX_3(NO)L_2$ (X = Cl,Br,I ; L = PEt_3, Et_2PhP) for ruthenium (II). In addition, para-substituted phenyldiethylphosphine ligands (p-$QPhEt_2P$; Q = Me_2N, MeO, Cl) have been prepared and their complexes with ruthenium (II) of stoichiometry $RuX_3(NO)L_2$ have been studied. The electronic effects of the para-substituents can be correlated with changes in spectroscopic parameters such as the nitrosyl infra-red stretching frequency and the energy of halogen to metal charge transfer transitions in the ultra-violet region.

The overall results for these three systems have been

compared and contrasted, and a general conclusion is that although σ bonding is the major component of the covalent contribution to the metal - halogen bond, the existence of a component of metal to halogen $M_{d\pi} \longrightarrow X_{d\pi}$ bonding appears to be the best explanation for a number of trends observed in the spectroscopic data.

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CHAPTER 1

INTRODUCTION

The work described in this thesis is concerned with spectroscopic studies on three distinct but related types of transition metal phosphine complexes containing halogeno-ligands. The three types are -

(a) four-coordinate MX_2L_2 and $M_2X_4L_2$ complexes,

(b) MOX_3L_2 and MNX_2L_3 octahedral complexes, and

(c) $MX_3(NO)L_2$ octahedral complexes,

where L = tertiary phosphine, X = halogen, and M is a range of metal ions. The foremost aim in the work was to investigate the nature of the metal-halogen bond, and, because of the choice of systems, the nature of the metal-phosphorus bond could be studied as well.

Emphasis has been given to a systematic approach as much as this is possible. Parameters such as the nature of the metal and its oxidation state, the phosphines, the halogeno-ligands, and the stereochemistry of the complexes have been varied within a series and between the three different types of complexes. Trends in the spectral properties have been related to these changes and where possible to the nature of the metal-halogen and metal-phosphorus bonds.

SECTION 1.1. SPECTROSCOPIC TECHNIQUES

The spectroscopic techniques employed in these studies were those of ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance spectroscopy; electronic absorption spectroscopy in the visible and ultra-violet

regions; and both high frequency (4000 - 400 cm^{-1}) and low frequency (400 - 40 cm^{-1}) infra-red studies.

While NMR is a nuclear phenomenon its main utility is in relating the observed resonances to variations in electron density around the nucleus. Information concerning alterations in bonding is therefore accessible by this method since such alterations will give rise to changes in the electron distribution around the nucleus. Electronic absorption spectroscopy can, in ideal cases, provide information about the energy levels available to the bonding, non-bonding, and antibonding electrons of the complexes. High frequency infra-red studies are of use in the observation of trends in certain characteristic absorptions, such as those of nitrosyl, oxo, and nitrido ligands in the present work. Low frequency infra-red studies allow the observation of the fundamental stretching vibrations of the metal-halogen and the metal-phosphorus bonds. Comparisons within and between series of complexes of these vibrational parameters can give information about the relative strengths of the bonds.

SECTION 1.2. THE NATURE OF THE METAL-HALOGEN AND METAL-PHOSPHORUS BONDS.

It is pertinent at this stage to consider the possible orbital components of the metal-halogen and metal-phosphorus bonds, and to review briefly previous experimental and theoretical conclusions.

(1) The Nature of the Metal-halogen Bond

Covalent bonding between a halogen and a metal ion can be broken down into three distinct components as represented in Figure 1.1, and described as follows:

(a) Overlap of a halogen p orbital (or some linear combination

FIGURE 1·1

POSSIBLE COMPONENTS OF THE METAL-HALOGEN BOND

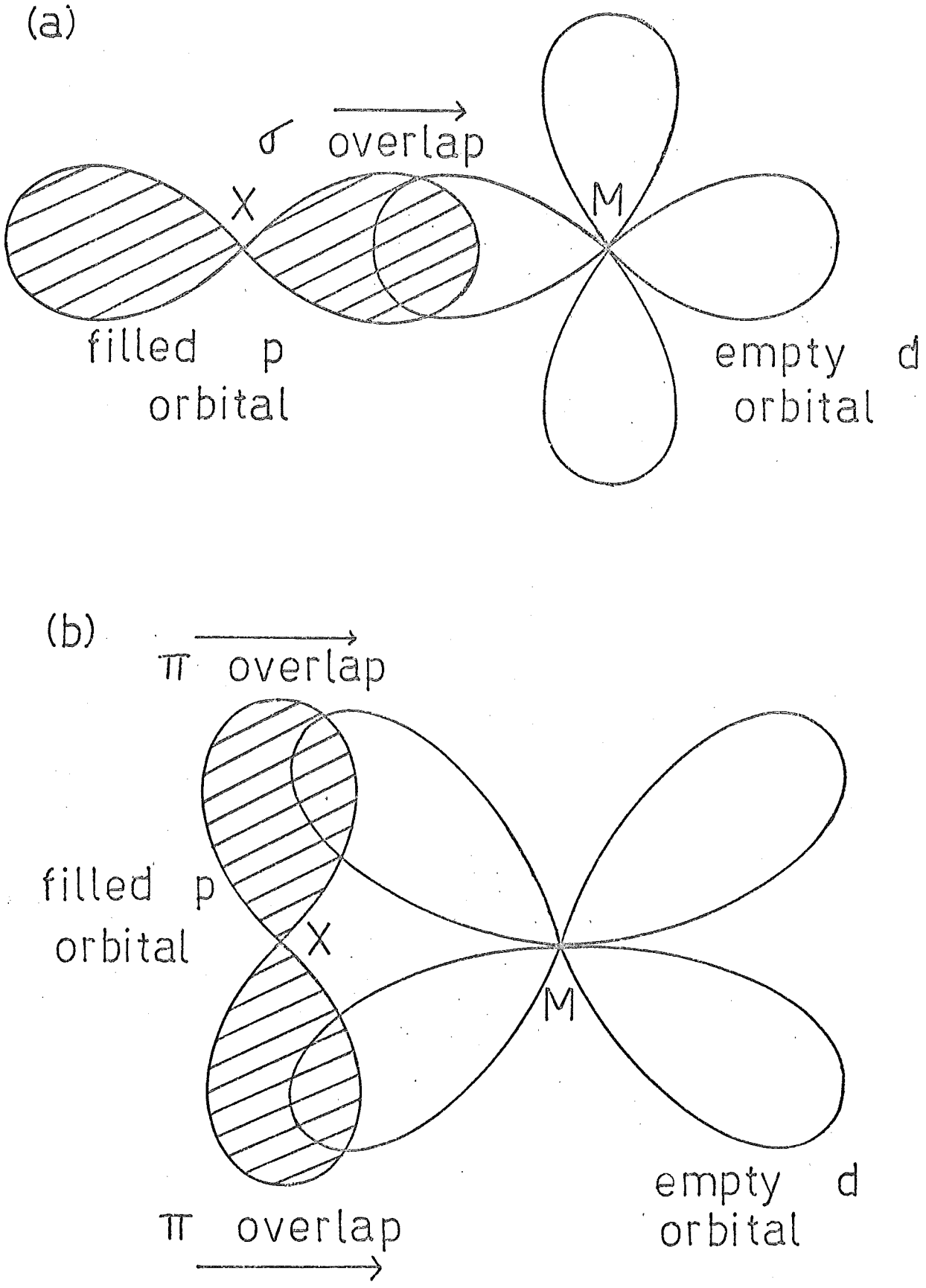
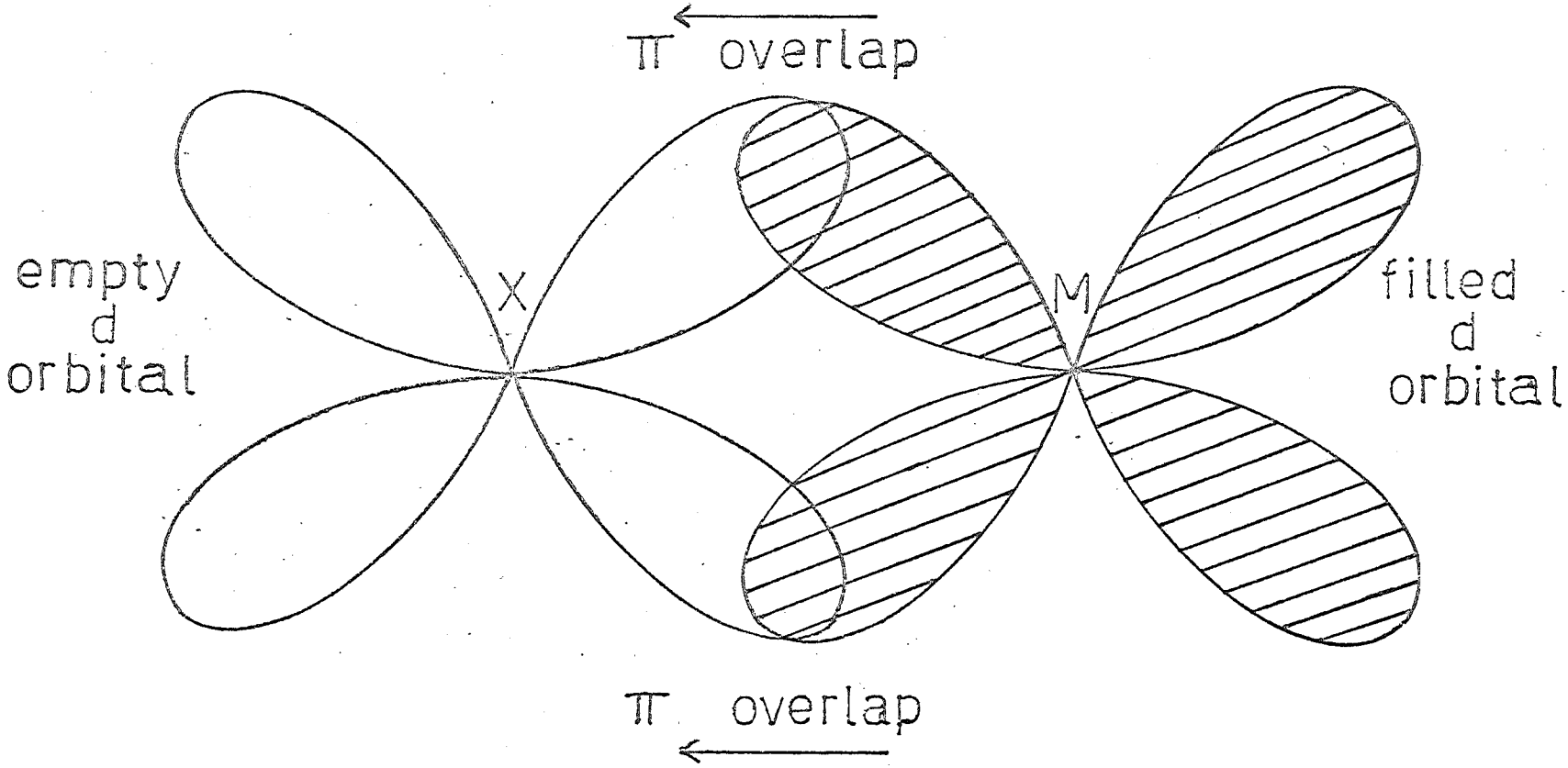


FIGURE 1·1 cont'd



of the halogen valence s and p orbitals) containing a lone pair of electrons, with a suitable empty metal orbital, or more probably with a linear combination of metal orbitals, such as s, p_x, p_y, $d_{x^2 - y^2}$ for a metal ion in a square planar complex. This results in the formation of a bond with σ symmetry.

(b) Overlap of either, or perhaps both, of the two filled halogen p orbitals remaining, with suitable available vacant metal d orbitals. This gives a π bond and the bonding interaction can be written as $X_{p\pi} \longrightarrow M_{d\pi}$, the arrow designating the direction of charge donation.

(c) Overlap of filled metal d orbitals with empty halogen d orbitals of suitable symmetry. This will give rise to a second type of π bond which can be written as $M_{d\pi} \longrightarrow X_{d\pi}$.

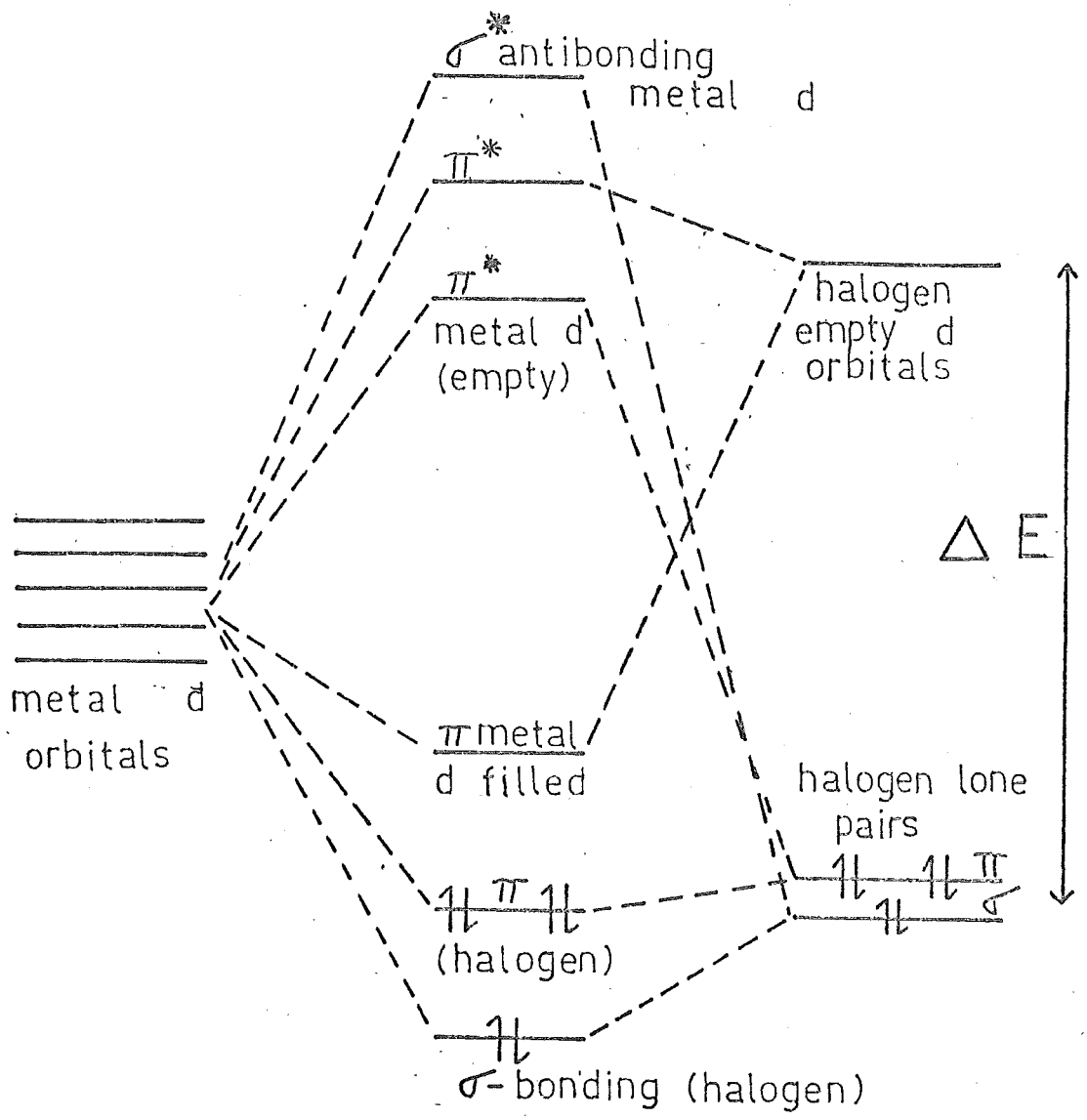
For the majority of metal-ligand bonds (there being a few notable exceptions, e.g. CO, NO) the σ bond (Figure 1.1 (a)) is considered to be the major component of the bonding, and this is probably also true for the halogens as ligands.

The degree to which the π bonds (b) and (c) above contribute to the metal-halogen bond, has been a subject of conjecture for some years. Many authors have, in fact, considered the importance of metal-halogen π bonding to be minor at best[1,2]. However, there is a considerable number of experimental observations which are best rationalised by invoking the existence of some π bonding component.

A qualitative energy level diagram representing the various bonding possibilities for the metal-halogen bond is given in Figure 1.2. Use will be made of this diagram later when indicating which of the types of bonding shown in Figure 1.1 have the potential of being adopted by each of the particular systems studied in the present work.

FIGURE 1·2

ENERGY LEVEL DIAGRAM FOR METAL-HALOGEN BOND COMPONENTS



(2) The Halogens as Ligands

Pearson's "hard" and "soft" acid-base criteria[3,4] provide a useful framework when considering differences between the halogens as ligands. Halogeno-ligands may thus be designated as soft bases (Br^-, I^-) or hard bases (F^-, Cl^-) in terms of the polarizability of the particular halogen. Thus fluorine in particular has a low polarizability[3] due to its small size and the difficulty in distorting its valence shell. Conversely the polarizability of the other halogens increases in the order Cl^-, Br^-, I^- mainly due to the increase in size in this order. Metal ions may also be classified as hard or soft in terms of whether they form more stable complexes with hard or with soft bases. Thus, soft acids in the Pearson formalism[4] are generally of large size, with a d^n configuration where $n \geqslant 6$, and in a low oxidation state. Chatt et al[5] consider that the important feature of soft acids is the presence of loosely held outer d electrons which can form π bonds by donation to suitable ligands with polarizable acceptor orbitals, such as occurs in the halogen soft bases Cl^-, Br^-, and I^-. On the basis of the foregoing discussion therefore, the ability of forming the $M_{d\pi} \longrightarrow X_{d\pi}$ bond should be in the order I > Br > Cl >> F and the opposite trend should exist for $X_{p\pi} \longrightarrow M_{d\pi}$ bonding.

Another way of investigating the relative ease of formation of $M_{d\pi} \longrightarrow X_{d\pi}$ bonds between a metal and a halogen is to consider the relative energy difference, ΔE, between the bonding p orbitals and vacant d orbitals (Figure 1.2) on the halogeno-ligands. The one electron orbital ionization energies of the free halogen atoms furnish a useful comparison of the relative energies of these orbitals. According to such data[6], the energy difference between the filled 2p and empty 3d orbitals in fluorine is 1550 kJ.

TABLE 1·1

POTENTIAL OF VARIOUS METAL IONS IN FORMING METAL-HALOGEN π BONDS

Electron configuration and stereochemistry	π-bonding potential	
d^8 square planar	no suitable empty d orbitals	no $M \xleftarrow{\pi} X$
	filled d orbitals	$M \xrightarrow{\pi} X$
octahedral d^6 Ru(II)	no suitable empty d orbitals	no $M \xleftarrow{\pi} X$
	filled d orbitals	$M \xrightarrow{\pi} X$
octahedral d^2 Re(V)	both empty and filled d orbitals	both $M \xleftarrow{\pi} X$ and $M \xrightarrow{\pi} X$ possible
octahedral d^5 Re(II)	half-empty suitable d orbital	both $M \xleftarrow{\pi} X$ and
	filled d orbitals	$M \xrightarrow{\pi} X$ possible

However, for the other halogens the energy difference (np - nd) is much less. Thus for chlorine the energy difference between the 3p and 3d levels is 1050 kJ, for bromine the 4p - 4d difference is 920 kJ, and for iodine the 5p - 5d difference is 710 kJ[6]. These energy differences show that of the halogens fluorine has the least accessible vacant d orbitals and that for the other halogens the possibility of forming $M_{d\pi} \longrightarrow X_{d\pi}$ bonds would increase in the order Cl < Br < I. In contrast the probable ease of formation for the other π bond, $X_{p\pi} \longrightarrow M_{d\pi}$, is considered to increase in the order I < Br < Cl $\ll$ F[6].

The possibility of formation of either, or both types of metal-halogen π bond discussed above is influenced by the d electron configuration of the metal. For the systems studied in the present work the d electron configurations range from d^8 (four-coordinate complexes), to d^6 (ruthenium (II) complexes), d^5 (rhenium (II) complexes), and d^2 (rhenium (V) complexes). Table 1.1 represents the various π bonding possibilities for each of these systems.

(3) Experimental and Theoretical Considerations on the Nature of the Metal-halogen Bond

The conclusions of previous workers, from both experimental and theoretical considerations, on the nature of the metal-halogen bond are represented briefly in tabular form as set out below. This topic has been reviewed in detail previously[7,8], covering the period up until 1968.

Compound Type	Method of Investigation	Reference	Interpretation of results in terms of the nature of the metal-halogen bond
hexachloro-metallate (IV) complexes	Molecular orbital calculations	9	The model employed here considered only the σ bonds and $X_{p\pi} \longrightarrow M_{d\pi}$ interactions between chlorine and the metal.
Complexes with second and third row transition metal ions	General theoretical considerations	10, 11	The implication of both groups of workers was that $M_{d\pi} \longrightarrow X_{d\pi}$ bonding between metal and halogeno-ligands was theoretically possible in their respective bonding schemes.
hexachloro-metallate (IV) complexes	Low frequency infra-red spectral studies	7 and references therein	The stretching force constants of the metal-halogen bonds increase across the second and third transition metal series. This has been interpreted as supporting an increase in $M_{d\pi} \longrightarrow X_{d\pi}$ bonding as the number of d electrons increases.
hexahalogeno-metallate (IV) complexes	Raman spectral studies	12-14	The stretching force constants for the a_{1g} symmetric stretch (Raman-active) increase across the third transition series. This has been interpreted as supporting $M_{d\pi} \longrightarrow X_{d\pi}$ bonding. Intensity anomalies for Raman-active vibrations have also been considered to support $M_{d\pi} \longrightarrow X_{d\pi}$ bonding.

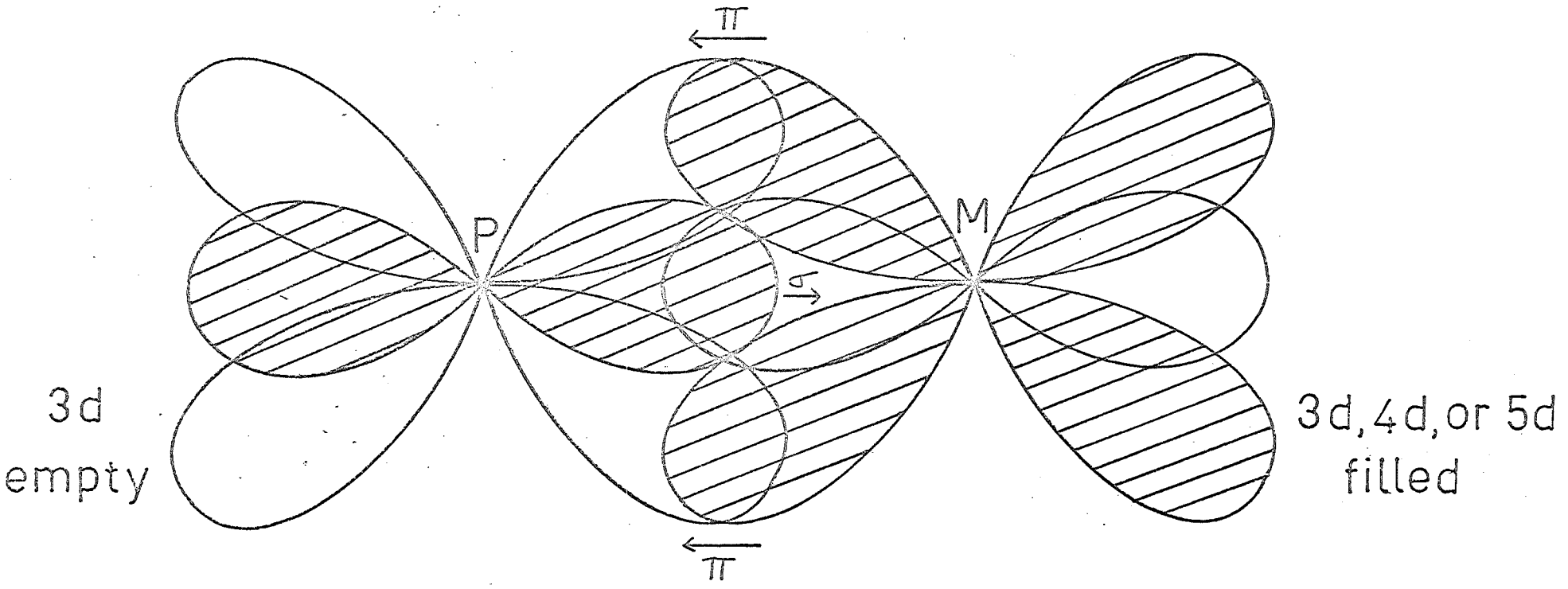
Compound Type	Method of Investigation	Reference	Interpretation of results in terms of the nature of the metal-halogen bond
hexahalogeno-metallate (IV) complexes with univalent cations	Correlation of low frequency infra-red data with unit cell size	15	Opposing trends in the correlation of infra-red frequencies with unit cell size for transition metal and non-transition metal MX_6^{2-} complexes were interpreted to support $M_{d\pi} \longrightarrow X_{d\pi}$ bonding.
The $IrCl_6^{2-}$ anion	Electron spin resonance and theoretical considerations	7, 16-18	The original workers[16-1] interpreted the ESR results from a theoretical standpoint to support 5% of $X_{p\pi} \longrightarrow M_{d\pi}$ interaction for each iridium-chlorine bond. The results have been reinterpreted[7] as also supporting $M_{d\pi} \longrightarrow X_{d\pi}$ bonding.
hexachloro-metallate (III) and (IV) complexes	Nuclear quadrupole resonance studies and theoretical considerations	19, 20-22	The results were interpreted in terms of the σ and $X_{p\pi} \longrightarrow M_{d\pi}$ components of the metal-halogen bond.
hexahalogeno-metallate (IV) anions	Magnetic studies of super-exchange phenomena	23, 24	A significant degree of $X_{p\pi} \longrightarrow M_{d\pi}$ bonding was considered as the reason for results obtained.

Compound Type	Method of Investigation	Reference	Interpretation of results in terms of the nature of the metal-halogen bond
hexahalogeno-metallates	Thermal stabilities of the compounds	7	The comparison of a considerable body of data on the thermal stabilities of complex chlorides was interpreted as supporting the existence of $M_{d\pi} \longrightarrow X_{d\pi}$ bonding as a factor in the relative stabilities of the complexes.
Dialkyl sulphide and selenide complexes of platinum group metals containing halogeno-ligands	^{1}H NMR studies	25, 26	Deshielding phenomena with change in halogeno-ligands have been inter-preted as supporting an increased component of $M_{d\pi} \longrightarrow X_{d\pi}$ bonding in these complexes.
Square planar platinum complexes with pyridine and halogeno-ligands	^{1}H NMR studies	27	The chemical shifts of proton resonances of the pyridine ligands varied in a manner which was considered to support a $M_{d\pi} \longrightarrow X_{d\pi}$ interaction.

It is not possible to draw any conclusions concerning the dominance of one type of π bond over the other from the information listed above. In most of the above studies only one spectroscopic technique has been employed, and these are often predisposed towards a particular conclusion. For example, the interpretation of NQR results for hexahalogenometallates[19,20-22] has generally been in terms of a modified Townes-Dailey approach[19] in which the

FIGURE 1·3

POSSIBLE COMPONENTS OF THE
METAL-PHOSPHORUS BOND



quadrupole coupling constants are related by an expression containing parameters for the ionic character of the bond, the s character of the halogen orbital, and the $X_{p\pi} \longrightarrow M_{d\pi}$ π bonding component. Possible $M_{d\pi} \longrightarrow X_{d\pi}$ interactions are not considered at all in this treatment.

The present work represents an attempt to extend the scope of investigations on the nature of the metal-halogen bond by employing a variety of spectroscopic techniques and a variety of distinct systems which are, nevertheless, interrelated (see Section 1.3, p.11).

(4) The Nature of the Metal-phosphorus Bond

Until about a decade ago the general consensus of opinion was that the metal-phosphorus bond could be adequately described by the proposals put forward by Chatt and co-workers[28-31]. Chatt's group had made the original suggestion that, besides a normal σ component involving a phosphorus orbital containing a lone pair of electrons overlapping with a suitable vacant metal orbital, a component of π back-donation from metal d orbitals to empty phosphorus 3d orbitals was also probable. The proposed bonding scheme is represented diagrammatically in Figure 1.3. It should be noted that a phosphorus $\longrightarrow$ metal π bond is not possible as there are no further lone pairs available on the phosphorus of R_3P ligands.

This type of metal to phosphorus back-donation has two important effects. The first of these is that there is an enhancement of the σ bonding properties of the phosphorus lone pair by an inductive effect of the metal d electrons delocalized on to the phosphorus atom. This effect has been termed "the synergic effect" in that the σ and π components augment each other.

The second result of the Chatt proposal was that it explained very well why phosphine (and related) ligands could stabilize the central metal ion in low oxidation states. The ability of the metal ion to transmit excess charge via delocalization on to the phosphorus atoms of the ligands by the back-donation mechanism is a stabilizing influence in low oxidation state situations[32].

In 1966 Pidcock, Richards and Venanzi[33] published results on ^{31}P NMR studies of some platinum (II) and platinum (IV) complexes, from which they concluded that the bonding of phosphines in low oxidation state complexes could be explained adequately by invoking the postulate that strong σ bonds were responsible for the observed effects, and that π bonding, if it occurred at all, was of negligible importance. Venanzi has since discussed these results in a more generalised manner[34].

The "σ-only" theory[33] evolved from the consideration of results from ^{31}P NMR spectroscopy. The utility of this theory therefore depends on whether or not it can explain a large number of experimental results which have been explained previously in terms of π bonding. For example, the π bonding argument has been used to explain the trans effect[35], the greater magnitude of the ^{195}Pt - ^{31}P coupling constants in cis complexes relative to trans isomers of platinum (II)[36]; the relative thermodynamic stabilities of cis and trans isomers of platinum (II)[30]; and fluorine chemical shifts in fluorophenylplatinum complexes[2]. Also, the shorter phosphorus-platinum distance in cis - $PtCl_2(PMe_3)_2$ compared with that of the trans isomer may be explained by π bonding, although the original investigators were reluctant to do this[37]. Pidcock[38] has discussed in some detail how the σ-only theory can be applied to the explanation of these and similar

problems. However, Grim and co-workers[39-41] have shown that the magnitude of ^{31}P - ^{195}Pt coupling constants in platinum (II) complexes, the original basis for the σ-only theory, can be interpreted equally as well to support π bonding arguments, Pidcock[38] has challenged Grim's interpretations, but the problem is still unresolved.

Mason and co-workers[42,43] have related metal-phosphorus bond lengths to oxidation state and electronic configuration in a series of tertiary phosphine complexes of third row transition metals, of general formula MCl_4L_2 and MCl_3L_3. The decrease in M-P bond length per unit increase in the electron configuration is consistently about 5 pm. In contrast the M-Cl bond length varies only slightly in the series. The results were discussed[43] in terms of the variation of σ covalent radii with change in hybridisation for the atoms involved.

SECTION 1.3. DETAILS OF SYSTEMS STUDIED IN THIS WORK

Past studies of the nature of the metal-halogen bond have been mostly concerned with hexahalogeno complexes of the transition metals. In order to widen the scope it was considered useful to choose a system which contained other ligands as well as halogens. Thus, the work described in this thesis is concerned with studies of tertiary phosphine transition metal complexes containing halogeno-ligands. Although the primary aim of this work was the study of the metal-halogen bond the choice of system gave the added advantage of the study of the metal-phosphorus bond in a variety of environments.

These complexes have several inherent advantages from the point of view of spectroscopic studies. The first of these is that a wide variety of phosphine complexes have been prepared and

characterised previously[44]. This previous work has been of assistance in enabling as complete a series of complexes as possible to be prepared, and hence allowing fuller comparisons of trends in spectroscopic parameters.

The second advantage is that with such a variety of possible systems for study one can select systems that give the widest possible range of parameters such as stereochemistry, oxidation state, metal, and phosphine.

Finally the nature of the chosen systems was such that they gave the best possible advantage to spectroscopic studies. Thus most compounds were diamagnetic which is important, although not necessarily essential, for NMR studies. The tertiary phosphines used in this work, mostly triethylphosphine (PEt_3) and diethylphenylphosphine (Et_2PhP), lead to compounds of adequate solubility for NMR and electronic spectral studies. Solubility has also been a hindrance, however, in a few cases where the complexes were too soluble to isolate as solids or required careful chromatographic procedures to remove excess of reagents.

With these considerations in mind the following systems were studied:

(1) Complexes of the type MX_2L_2 which contain a four-coordinate metal ion in either a square planar or a tetrahedral environment. M was Co (II) or Zn (II) for the tetrahedral complexes, and Ni (II), Pd (II), or Pt (II) for the square planar complexes. The halogeno-ligand was one of Cl, Br, or I, and the phosphine ligand was either PEt_3 or Et_2PhP. Binuclear $M_2X_4L_2$ complexes containing four-coordinate square planar Pd (II) and Pt (II) have also been studied. Triethylphosphite complexes of Pt (II) were also prepared. An unsuccessful attempt to prepare some rhodium (I) square planar complexes is also described.

(2) Rhenium phosphine complexes containing oxo, nitrido, or nitrosyl ligands. The metal ions in these complexes have the electronic configuration d^2 for Re (V) oxo and nitrido complexes, and d^5 for Re (II) nitrosyl complexes. The nitrosyl complexes have also been investigated from a preparative standpoint, and the complexes in general have been studied spectroscopically. Some technetium complexes were also prepared in order to see whether or not the phosphine complex chemistry of technetium parallels that of rhenium.

(3) Ruthenium phosphine complexes of the (II) and (III) oxidation states. The Ru (III) complexes were of the form RuX_3L_3 and have been compared with the nitrosyl Ru (II) complexes of form $RuX_3(NO)L_2$ (X = halogen, L = phosphine). In addition a series of para-substituted phenyldiethylphosphine ligands has been prepared and their Ru (II) nitrosyl complexes have been studied spectroscopically. The para substituents were Me_2N, MeO, Cl, and H (the latter being the unsubstituted Et_2PhP ligand), thus giving a range of electronic effects which can be transmitted via the bonding system. Correlations of the electronic effects of these substituents with changes in spectroscopic parameters have been made.

The results obtained for the three systems are discussed in Chapters 2, 3 and 4 respectively. These chapters also contain general theoretical discussions and brief reviews of previous work where appropriate. Chapter 5 contains a summary of the results and general discussion of these findings in terms of the nature of the metal-halogen and metal-phosphorus bonds.

CHAPTER 2

SPECTROSCOPIC STUDIES ON SOME FOUR-COORDINATE METAL COMPLEXES

The work described in this Chapter is principally concerned with spectroscopic studies on some metal phosphine complexes containing halogeno ligands, with the metal ion in four-coordination. The preparations of the complexes are also discussed together with attempts to prepare rhodium (I) square planar complexes of triethylphosphine by a number of methods.

The complexes studied here may be divided into the following classes ;

(a) MX_2L_2 square planar complexes, where M is Ni, Pd or Pt; X is Cl, Br or I; and L is PEt_3, Et_2PhP, and sometimes $P(OEt)_3$.

(b) $M_2X_4L_2$ binuclear planar complexes where M is Pd or Pt; X is as above; and L is PEt_3 or Et_2PhP.

(c) MX_2L_2 tetrahedral complexes where M is Co or Zn; X is again as above; and L is PEt_3 or Et_2PhP.

These complexes have been studied in this work by far infra-red, ^1H, ^{13}C, ^{31}P NMR and electronic absorption spectroscopy.

It is relevant first to consider previous work in this general area.

SECTION 2.1. INTRODUCTION

Phosphine complexes of the type considered here have been reviewed recently.[44,45] The following discussion is limited to those aspects of previous work that have relevance to this study.

(a) Nickel (II) complexes:-

Trialkylphosphines react with nickel halides to form diamagnetic complexes, $NiX_2(PR_3)_2$, which are red or brown in colour.[46-49] Jensen[48] showed that the complexes had a trans square planar stereochemistry from dipole moment measurements and the diamagnetism of the compounds. This has been confirmed by a single crystal X-ray structure determination[50] of $NiBr_2(PEt_3)_2$ in which Ni-Br = 230 pm, Ni-P = 226 pm, and the bond angle BrNiP is close to 90°. Trimethylphosphine forms four - or five - coordinate complexes.[46,47] Triphenylphosphine forms blue paramagnetic four-coordinate complexes which have been shown to be tetrahedral.[51]

The complexes of mixed alkyl-aryl phosphines are of interest in that they exist in solution, and in some cases in the solid state, as a mixture of planar and tetrahedral forms.[52,53] Thermodynamic and kinetic studies of the planar $\rightleftharpoons$ tetrahedral equilibrium have been carried out using ^1H NMR, electronic spectra and magnetic measurements.[54]

The four coordinate bis phosphine complexes have been extensively studied spectroscopically. In particular far infra-red spectroscopy has been used to determine the stereochemistry of $NiX_2(PR_3)_2$ complexes.[55-57] Studies by Nakamoto and co-workers on metal isotope effects in the far infra-red have led to unambiguous assignments[57] of the stretching modes ν (Ni-P) and ν (Ni-X). The electronic spectra of nickel phosphine complexes have been widely used to distinguish between the tetrahedral and square planar structures possible for $NiX_2(PR_3)_2$, and these have been reviewed by Sacconi.[58]

(b) Palladium (II) and platinum (II) complexes:-

Palladium and platinum form an extensive series of phosphine complexes in the divalent state and platinum also forms quadrivalent phosphine complexes. The palladium (II) and platinum (II) complexes have been comprehensively studied, mainly as a result of work by Chatt and his research group, who have done much pioneering work in the field of phosphine and arsine chemistry in general and with these two elements in particular.

(i) Cis and trans - $MX_2(PR_3)_2$ complexes.

Cis and trans isomers of diamagnetic planar d^8 $MX_2(PR_3)_2$ complexes are generally white, yellow or orange in colour. The cis and trans isomers have been assigned on the basis of dipole moment measurements, and more recently from spectroscopic studies. Both platinum (II) isomers can be obtained quite readily; however cis complexes of palladium are rather rare and have been obtained only recently.

In the platinum series cis and trans isomers are formed in admixture on reaction of PtX_4^{2-} with PR_3.[59] The separation of these isomers can be achieved by the following procedures.[60] The pure cis isomer is obtained by suspending the crude mixture of isomers in warm light petroleum. Evaporation of the solvent leads to the selective precipitation of the cis isomer before the trans. The trans isomer can be obtained by dissolving the crude complex in benzene containing a trace of the ligand. This affords an equilibrium mixture in which the trans isomer predominates. The addition of a trace of the binuclear complex, $Pt_2X_4(PR_3)_2$, reacts with the excess phosphine present in solution, giving two moles of the mononuclear trans complex and effectively freezing the equilibrium. The trans isomers are then obtained

by evaporation of the solvent and recrystallisation from light petroleum. In this way Chatt and Wilkins[60] isolated cis and trans - $PtCl_2(PPr^n_3)_2$. Subsequently they studied the thermodynamics of the equilibrium,

cis - $PtCl_2(PEt_3)_2 \rightleftharpoons$ trans - $PtCl_2(PEt_3)_2$, calculated ΔG, ΔH, and ΔS and found that the total bond energy of the cis isomer is approximately 42 kJ > the trans. The equilibrium shifts in favour of the trans in the series Cl < Br < I.[61] The mechanism of the phosphine - catalysed isomerisation of cis - $PtCl_2(PR_3)_2$ (R = ^{n}Pr, ^{n}Bu) has recently been reexamined.[62] The reaction is first order and involves a five-coordinate transition state. Other workers[63,64] have used ^{1}H NMR spectroscopy to study the cis-trans isomerisation of both palladium (II) and platinum (II) complexes in solution.

The structures of several $MX_2(PR_3)_2$ complexes have been determined by single crystal X-ray crystallographic studies. For example Messmer and Amma[65] studied trans - $PtX_2(PEt_3)_2$ (X = Cl,Br) and found the Pt, P and X atoms to be essentially square planar, with Pt-P = 229.8 pm (Cl) and 231.5 pm (Br), Pt-Cl - 229.4 pm, Pt - Br = 242.8 pm. The structure of cis - $PtCl_2(PMe_3)_2$ is also planar, but with a small distortion towards tetrahedral.[37] Similarly cis - $PdCl_2(Me_2PhP)_2$ exhibits a small distortion from coplanar square geometry.[66]

The complexes have been studied extensively by spectroscopic techniques. The far infra-red spectra of trans - $MX_2(PR_3)_2$ complexes have been used to determine stereochemistry and to assign ν (M-X) and ν (M-P) vibrations.[57,67-69]. The Raman spectra of the complexes have also been reported and discussed.[69,70].

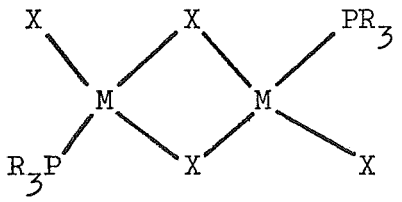
A large range of compounds have been studied by ^{1}H[63,71,72],

^{13}C[73,74] and ^{31}P[40,64,75-77] NMR spectroscopy, and Fryer and Smith[78] have reported the ^{35}Cl NQR spectra of some $MCl_2(PR_3)_2$ complexes.

Electronic spectra of mononuclear square planar palladium (II) and platinum (II) complexes have not been extensively studied[97] and the charge transfer region of these spectra has been only briefly discussed.

(ii) Halogen-bridged binuclear complexes. The halogen-bridged binuclear complexes have the form $M_2X_4(PR_3)_2$. They may be prepared by several methods, for example fusing $MX_2(PR_3)_2$ with K_2MX_4,[79-81] or by slurrying these reactants in a hydrocarbon solvent.[82]

The complexes have the structure



and no other isomers have thus far been observed.[80,81] The single crystal X-ray structure of the platinum complex with PPr^n_3 as ligand has been determined.[83]

Spectroscopic studies on these binuclear bridged complexes have involved the use of ^{31}P NMR[64] and far infra-red spectroscopy.[69,84,85]

(c) Cobalt (II) complexes:-

Cobalt (II) halides react with tertiary phosphines to form tetrahedral complexes of general formula CoX_2L_2. In these complexes cobalt has the d^7 configuration.

Jensen[86] isolated blue $CoCl_2(PEt_3)_2$ which had a dipole

moment of 8.7D, indicating either a cis square planar or a tetrahedral structure. Subsequently[87] the magnetic moment determination (μ_{eff} = 4.39 B.M.) indicated three unpaired electrons and confirmed a tetrahedral stereochemistry.

The complexes have been most extensively studied from the point of view of their electronic spectra,[87-89] both in the charge transfer and ligand field regions.

(d) Zinc (II) complexes:-

Zinc halides form 1:2 complexes with tertiary phosphine ligands. These are obtained by direct reaction in water, alcohols, or ether.[90-92] The complexes have tetrahedral structures and increase in stability towards ligand dissociation in the series Cl < Br < I. Coates et al[90] investigated the factors affecting this stability and suggested that they could be related to the base strengths of the phosphine ligands.

The compounds have received some study using far infra-red spectroscopy[93-96] and dipole moments have also been measured.[92]

SECTION 2.2 RESULTS AND DISCUSSION

2.2.1 Low Frequency Infra-Red Spectra

Introductory comments:-

The far infra-red spectra of some four-coordinate dihalogeno complexes of Co(II),Ni(II),Pd(II), and Pt(II) with triethylphosphine and diethylphenylphosphine have been recorded in the present work. A considerable number of papers dealing with the far infra-red spectra of these complexes has been published;[55,67-69,85,98] however some previous assignments have been shown to be in error by the work of Nakamoto and Shobatake.[57] The advantage of the method of these workers is that metal

isotopes were used in order to determine which vibrations involved the metal ion. Nakamoto and Shobatake concluded[57] that previous assignments of metal-halogen stretching and bending vibrations were correct, but that previous assignments of metal-phosphorus stretching vibrations had been made in error. Thus these workers[57] presented revised assignments for far infra-red absorptions of the complexes $NiCl_2(PEt_3)_2$, $NiBr_2(PEt_3)_2$, and $PdCl_2(PEt_3)_2$, using the isotopic substitution method. The work to be discussed in this section is concerned with the extension of these revised assignments to cover all the compounds studied in the present work.

Spectral assignments for square planar complexes

(a) General:-

The normal modes of vibration expected for cis and trans mononuclear complexes, and binuclear halogen-bridged complexes, can be calculated using group theory (see later discussion). In order to make these calculations the phosphine ligands are considered as point masses, thus considerably simplifying the procedure. This simplification however introduces approximations into the resulting theoretical descriptions of the vibrational modes, in that vibrations involving the carbon atoms of the tertiary phosphine ligands cannot be derived. Thus the spectra show more absorptions than are expected on a theoretical basis and in the present work a number of these extra absorptions have been assigned, as follows.

(i) Internal ligand vibrations:- To enable as complete an assignment as possible to be made knowledge of the vibrational spectra of the free ligands are important. Certain absorptions present for the free ligands are reported as undergoing little or no modification upon coordination,[100] and

absorptions around 380 cm^{-1} and 330 cm^{-1} (PEt_3), and 385 cm^{-1} and 360 cm^{-1} (Et_2PhP) are assigned on this basis. The absorptions are generally of weak intensity. Other vibrations assigned as internal ligand modes are listed in the Tables.

(ii) The in-plane metal-phosphorus-carbon bending mode:- An absorption, which has been the subject of conflicting assignments in the past, is observed in the present work in the infra-red spectra of the square planar complexes, in the region 180 $\pm$ 20 cm^{-1} (PEt_3 complexes) and 170 $\pm$ 10 cm^{-1} (Et_2PhP complexes). This band is at least of medium intensity in all spectra, and in some cases is the strongest absorption observed in the spectrum. In all previous work [57,67-69,85] this band has been assigned as an internal ligand vibration.

Clark et al.[99], in studies of the far infra-red spectra of dialkyl sulphide complexes of palladium (II), assigned a similar medium to strong absorption, which occurred in the spectra of all the complexes studied over a narrow frequency range (200 to 220 cm^{-1}), to the in-plane metal-sulphur-carbon bending vibration. The band in question had previously been assigned[101] to the δ(S-Pd-S) bending mode but such an assignment is not possible for the bridged binuclear complex, trans - $(Me_2S)ClPdCl_2PdCl(SMe_2)$, which also has a strong absorption band at 208 cm^{-1}.[99]

Thus the absorption band in the 160 - 200 cm^{-1} region of the spectra obtained in the present work is assigned, analogously to the assignment in the sulphide complexes, to the in-plane metal-phosphorus-carbon bending mode, designated δ(MPC). As noted above the appearance of this band in the infra-red spectra cannot be predicted from theoretical considerations since, in these treatments, the ligand is considered as a point mass.

Two lines of evidence indicate that the metal is involved in the vibration. Firstly, the position of the absorption is dependent on the mass of the central metal atom. For PEt_3 complexes the absorption in the trans - nickel complexes occurs at higher than 190 cm^{-1}, while for the trans - palladium and platinum complexes it occurs some 10 cm^{-1} lower (see Table 2.1). For Et_2PhP complexes (Table 2.3) the same relative change is observed with the band observed at 170 cm^{-1} for the trans - nickel complexes and 160 cm^{-1} for the trans - palladium compounds.

Secondly, the metal isotope work of Nakamoto and Shobatake[57] is of assistance here. These workers did not assign the strong band, which they observed at 180 $\pm$ 20 cm^{-1} for PEt_3 complexes of nickel and palladium, to δ (MPC); instead they followed previous assignments[69] to an internal ligand mode. However the data of the Japanese workers[57] shows that the 180 $\pm$ 20 cm^{-1} mode is subject to change upon isotopic substitution. The shifts are small, as might be expected for bending vibrations. However they are still greater than those observed for internal ligand modes.[57] Thus the band at 183.8 cm^{-1} undergoes a shift of 1.8 cm^{-1} on substitution of ^{104}Pd for ^{110}Pd in $PdCl_2(PEt_3)_2$.[57] This is greater than the 0.5 cm^{-1} and 1.0 cm^{-1} changes produced in the δ (X-M-X) and δ (P-M-P) bending modes by isotopic substitution in $PdCl_2(PEt_3)_2$. The shift of 1.8 cm^{-1} in the 183.8 cm^{-1} absorption seems too large to allow the metal to be ruled out of participation in the vibration, although a sizeable contribution could occur by coupling with the adjacent (234.5 cm^{-1}) metal - phosphorus asymmetric stretching vibration. Such coupling is less likely to occur for the analogous nickel complexes since the energy difference between the nickel - phosphorus stretching mode and the bending vibration

under discussion is c a. 70 cm^{-1} in both chloro and bromo complexes. However, the absorption at 200.2 cm^{-1} for $^{58}NiCl_2(PEt_3)_2$ undergoes a shift of 0.8 cm^{-1} on change to ^{62}Ni and the 190.4 cm^{-1} absorption of $^{58}NiBr_2(PEt_3)_2$ shifts by 0.7 cm^{-1}.[57] Considering that absorptions which are not assigned as involving the metal atom in the associated vibration show virtually no change upon isotopic substitution the above considerations may be taken as evidence that the metal is indeed involved in the 180 $\pm$ 20 cm^{-1} vibrational absorption of PEt_3 complexes.

The above discussion in terms of metal isotope effects considers PEt_3 complexes only. However it seems reasonable to conclude by analogy that the 170 $\pm$ 10 cm^{-1} absorption in <u>trans</u> - Et_2PhP complexes can also be assigned to an in-plane metal-phosphorus-carbon bending vibration. The slight shift in position in the Et_2PhP complexes relative to the PEt_3 complexes could be expected on the basis of the different phosphines involved.

A second intense absorption in the far infra-red spectra of Et_2PhP complexes is also of interest. For <u>trans</u> - nickel complexes this band occurs near 235 cm^{-1} and, on change to palladium, it is observed near 200 cm^{-1}. This change suggests once again that the metal is involved in the vibration and it seems reasonable to conclude that the absorption corresponds to a second type of metal-phosphorus-carbon bending mode, this time involving the carbon of the phenyl ring, rather than of the ethyl groups, of the ligand.

(iii) <u>Out-of-plane molecular deformations and lattice-vibrations</u>:- Characteristic absorptions of the complexes which occur in the range 120-80 cm^{-1} have been previously assigned[69] as out-of-plane ligand deformations.

TABLE 2.1

Infra-red active normal modes of vibration for *trans*-square planar MX_2L_2 complexes[102]

Symmetry	Approximate Description	Number expected
B_{3u}	asymmetric M-X stretching	1
B_{2u}	asymmetric M-P stretching	1
B_{1u}	out-of-plane metal-halogen bending, π (X-M-X)	1
B_{1u}	out-of-plane metal-phosphorus bending, π (P-M-P)	1
B_{2u}	in-plane metal-halogen bending δ (X-M-X)	1
B_{3u}	in-plane metal-phosphorus bending, δ (P-M-P)	1

However this assignment is in doubt as the absorptions are often of medium intensity, and it may be more realistic therefore to assign them to the out-of-plane π (MPC) vibration, the analogue of the in-plane metal-phosphorus-carbon bending mode, δ (MPC), discussed above. The Japanese workers[57] preferred to make no assignment for these absorptions and, in fact, the effect of metal isotope substitution in this case is comparable to the effect on internal ligand modes. Clark et al.[99] noted the probability of the existence of a π (MSC) mode in the dialkyl sulphide studies, but did not make an assignment.

Lattice vibrations of varying intensity, but generally weak, are observed for most complexes; only the strongest of these vibrations have been included in the tables. The absorption profile is dependent on the nature of the mull, but absorption positions do not change.

(b) Infra-red assignments of metal-ligand vibrations for mononuclear trans complexes:-

Treating the phosphine ligands as point masses the infra-red active normal modes of vibration for mononuclear trans complexes (D_{2h} symmetry) have been calculated to have the characteristics given in Table 2.1.[102] It did not prove possible to assign absorptions to the two expected B_{1u} out-of-plane bending modes in the present work. However the other expected infra-red active fundamentals given in Table 2.1 have been located and assigned. The compound trans - $PtI_2(Et_2PhP)_2$ was the only trans - platinum complex of Et_2PhP which could be obtained in a satisfactory crystalline state in the present work.

(i) Metal-halogen stretching vibration:- The one expected infra-red active metal-halogen asymmetric stretching vibration (B_{3u} symmetry) has been readily assigned, on the basis

of its strong intensity (except for iodides) and from a comparison of features in the spectra common to a series of compounds differing only in halogen. It is noteworthy that ν_a (M-X) is virtually invariant with change in phosphine (Tables 2.2, 2.3) in these trans complexes. A similar situation has been observed previously[68] for a much wider range of phosphine ligands. The spectra of most of the triethylphosphine complexes have been reported previously;[55,57,67-69] however the diethylphenylphosphine compounds have not been discussed before. The metal isotope substitution technique[57] confirms the previous assignments for ν_a(M-X) in PEt_3 complexes.

The only assignments which present any difficulty are those of ν_a(Ni-I) in the compounds $NiI_2(PEt_3)_2$ and $NiI_2(Et_2PhP)_2$. Neither complex has been considered in previous studies. However weak absorptions at 307 cm^{-1} (PEt_3 complex) and 302 cm^{-1} (Et_2PhP complex) are in the expected region for ν_a (Ni-I) and all other nearby absorptions can be satisfactorily assigned. Boorman and Carty[55] have assigned ν_a(Ni-I) in the complex $NiI_2(Me_2PhP)_2$ to a weak-medium band at 255 cm^{-1}. This seems more likely to correspond to ν_a(Ni-P) on the basis of the isotopic work of Nakamoto and Shobatake[57] (see below).

(ii) Metal-phosphorus stretching vibration:- Previous assignments[55,67-69] of the one expected infra-red active metal-phosphorus asymmetric stretching vibration (B_{2u} symmetry) have been made in error, as shown by the isotopic studies of the Japanese workers.[57] Having regard to the assignments made by these workers for the three complexes $NiCl_2(PEt_3)_2$, $NiBr_2(PEt_3)_2$ and $PdCl_2(PEt_3)_2$, similar assignments can be made for the complexes studied in the present work. Thus a band near 265 cm^{-1} of medium intensity in the nickel complexes of PEt_3 can be

TABLE 2.2

Far Infra-Red Spectra : Assignments for mononuclear trans triethylphosphine complexes

frequencies in cm^{-1}

BAND ASSIGNMENT	$NiCl_2(PEt_3)_2$	$NiBr_2(PEt_3)_2$	$NiI_2(PEt_3)_2$	$PdCl_2(PEt_3)_2$	$PdBr_2(PEt_3)_2$	$PdI_2(PEt_3)_2$	$PtCl_2(PEt_3)_2$	$PtBr_2(PEt_3)_2$	$PtI_2(PEt_3)_2$
ν_a(M-X)	403s	338m	307w	356s	269m	218wm	340vs	252ms	201w
ν_a(M-P)	270s	263m	253m	235m	228m	(a)	230w	223ms	220w
δ(X-M-X)	185m	151wm	142m	165m	138w	130m	166m	159m,sh	145w
δ(P-M-P)	164w	(b)	(b)	145w	(b)	(b)	145wm	133w	132w,br
δ(MPC)	199ms	191s	184s	183s	176s	172s	183m	181ms	175vs
δ(CCP)	375wm	378wm	377w	380w	376w	380w	383w	383wm	386w
	365w		359w		360w	365w	363w		
	324wm	327m	329w	330wm	330m	330w		330m	333w
	249m	253sh		268w		250w	270w	283w	237m
π(MPC)	109s,br	106ms,br	95s	110br,m	100m,br	90m,br	115m	102m,br	94m,br
LATTICE	47w	(b)	50w	56w	55w	55wm	82w	85w	48wm
				47w	44w		48m	46w	

(a) masked

(b) no absorption assignable

TABLE 2.3

Far Infra-Red Spectra : Assignments for mononuclear *trans* diethylphenylphosphine complexes

frequencies in cm^{-1}

BAND ASSIGNMENT	$NiCl_2(Et_2PhP)_2$	$NiBr_2(Et_2PhP)_2$	$NiI_2(Et_2PhP)_2$	$PdCl_2(Et_2PhP)_2$	$PdBr_2(Et_2PhP)_2$	$PdI_2(Et_2PhP)_2$	$PtI_2(Et_2PhP)_2$
ν_a(M-X)	398m	336m	302wm	353s	270m	212w	202w
ν_a(M-P)	256s	261m	258m	248m	243m	240m	(b)
δ(X-M-X)	(a)	153w	138w	147w	133wm	146w	146w
δ(P-M-P)	(a)	140w	120w	(b)	111w	117m	(b)
δ(MPC ethyl)	176ms	170ms	166s	166ms	161ms	163ms	156m
δ(MPC phenyl)	240ms	236ms	232m	206ms	201s	198ms	(b)
δ(CCP)	381w	395m	394w	392w		398wm	395m
	345m		365w				377m
	317s	315s	319s	319ms	322m	313m	316s
					317m		
π(MPC)	120m	97m	95w	115wm	90m	91w	97w
LATTICE	66w	57w	85wm	86w			
				45w	46w	55wm	(b)

(a) masked

(b) no absorption assignable

TABLE 2.4

Infra-red active normal modes of vibration for *cis*-square planar MX_2L_2 compounds[102]

Symmetry	Approximate Description	Number Expected
A_1	symmetric M-X stretching	1
A_1	symmetric M-P stretching	1
B_1	asymmetric M-X stretching	1
B_1	asymmetric M-P stretching	1
$2A_1 + B_1$	in-plane bending modes	3
B_2	out-of-plane bending modes	1

assigned to ν_a(Ni-P). In the palladium PEt_3 complexes ν_a(Pd-P) is assigned to the band near 230 cm^{-1} and for platinum complexes of the same ligand ν_a(Pt-P) is assigned to the band near 255 cm^{-1}. The corresponding assignments for ν_a(Ni-P) in Et_2PhP complexes have been made to bands which are generally lower in energy than those for the PEt_3 complexes. (see Tables 2.2 and 2.3). This may reflect a small reduction in the coordinating power of Et_2PhP compared with PEt_3, on the basis of replacement of one ethyl group with a more electron-withdrawing phenyl group.

(iii) In-plane metal-halogen and metal-phosphorus bending vibrations:- The in-plane bending vibrations δ (X-M-X) (B_{2u} symmetry) and δ (P-M-P) (B_{3u} symmetry) give rise to absorptions in the 160 - 120 cm^{-1} region. It has not been possible to make assignments of these modes for all spectra (see Tables 2.2 and 2.3) since in some cases the absorptions are very weak and are not discernable above the background.

(c) Infra-red assignments of metal-ligand vibrations for mononuclear cis complexes:-

The MX_2P_2 skeleton for cis phosphine complexes has C_{2v} symmetry. The infra-red active normal modes of vibration[102] are given in Table 2.4.

According to Adams et al.[68] there is a likelihood of a substantial contribution from coupling of vibrations of the same symmetry in cis - MX_2L_2 complexes. Thus mutually trans metal-halogen and metal-phosphorus vibrations might be expected to interact with each other, particularly when the energies of these vibrations are of similar magnitude. Hence the observed absorption frequencies may be somewhat displaced from their expected positions. Bending modes will be similarly affected

TABLE 2.5

Far Infra-Red Spectra : Assignments for mononuclear cis triethylphosphine complexes

frequencies in cm^{-1}

BAND ASSIGNMENT	$PtCl_2(PEt_3)_2$	$PtBr_2(PEt_3)_2$	$PtI_2(PEt_3)_2$
ν_a(M-X)	279s	188s	150ms
ν_s(M-X)	303s	201sh	172m,sh
ν_a(M-P)	241m	(b)	(b)
ν_s(M-P)	260m	285ms	(b)
Bending Modes	157w	143w	135m
	145w	135w	
δ(MPC)	170m	(a)	160ms
	380wm	383w	388w
δ(CCP)	343w	331w	370wm
	230sh		332wm
	209w		315w
			230w
π(MPC)	114wm	115w,br	115ms,br
LATTICE	55wm,br	51w	90wm 43w

(a) masked (b) no absorption assignable

TABLE 2.6

Far Infra-Red Spectra : Assignments for mononuclear cis diethylphenylphosphine complexes

BAND ASSIGNMENT	frequencies in cm^{-1}			
	$PtCl_2(Et_2PhP)_2$	$PtBr_2(Et_2PhP)_2$	$PtI_2(Et_2PhP)_2$	$PdCl_2(Et_2PhP)_2$
ν_a(M-X)	281s	187m	157m,sh	292ms
ν_s(M-X)	313s	202m	168s	308s
ν_a(M-P)	222m	228w	235wm	222w
ν_s(M-P)	269ms	(b)	270m	257ms
Bending modes	(a)	(b)	125w	145wm 122wm
δ(MPC)	156m	(b)	(a)	160wm
δ(CCP)	356w	335w	346w	377w 352w
π(MPC)	(b)	115m,br	113m,br 82wm	(b) 80w
LATTICE	67w	57wm 50wm	58wm	45w

(a) masked (b) no absorption assignable

FIGURE 2·1

FAR INFRA-RED SPECTRA OF NICKEL(II) COMPLEXES

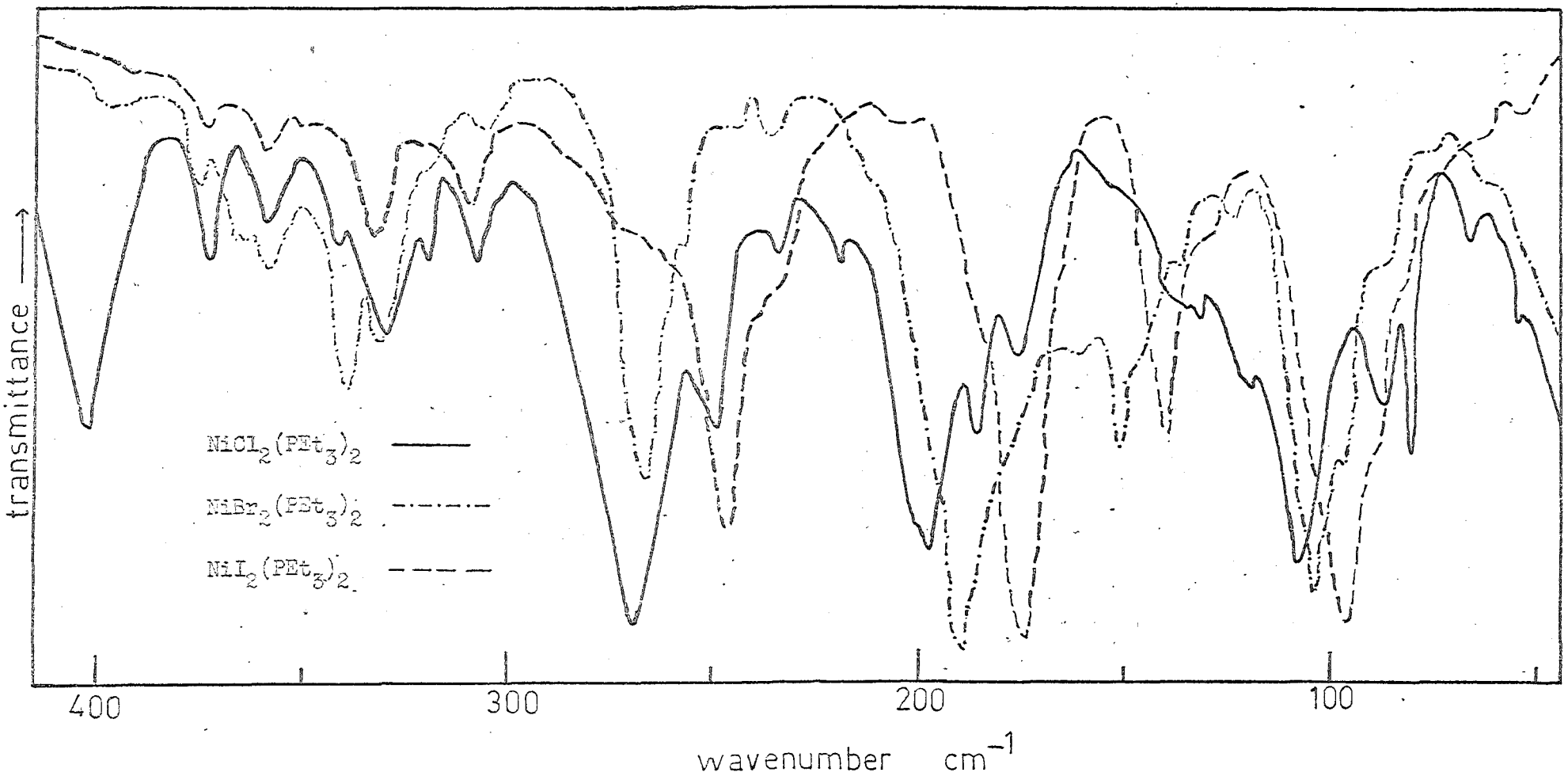


FIGURE 2·2

FAR INFRA-RED SPECTRA OF CIS-PLATINUM(II) COMPLEXES

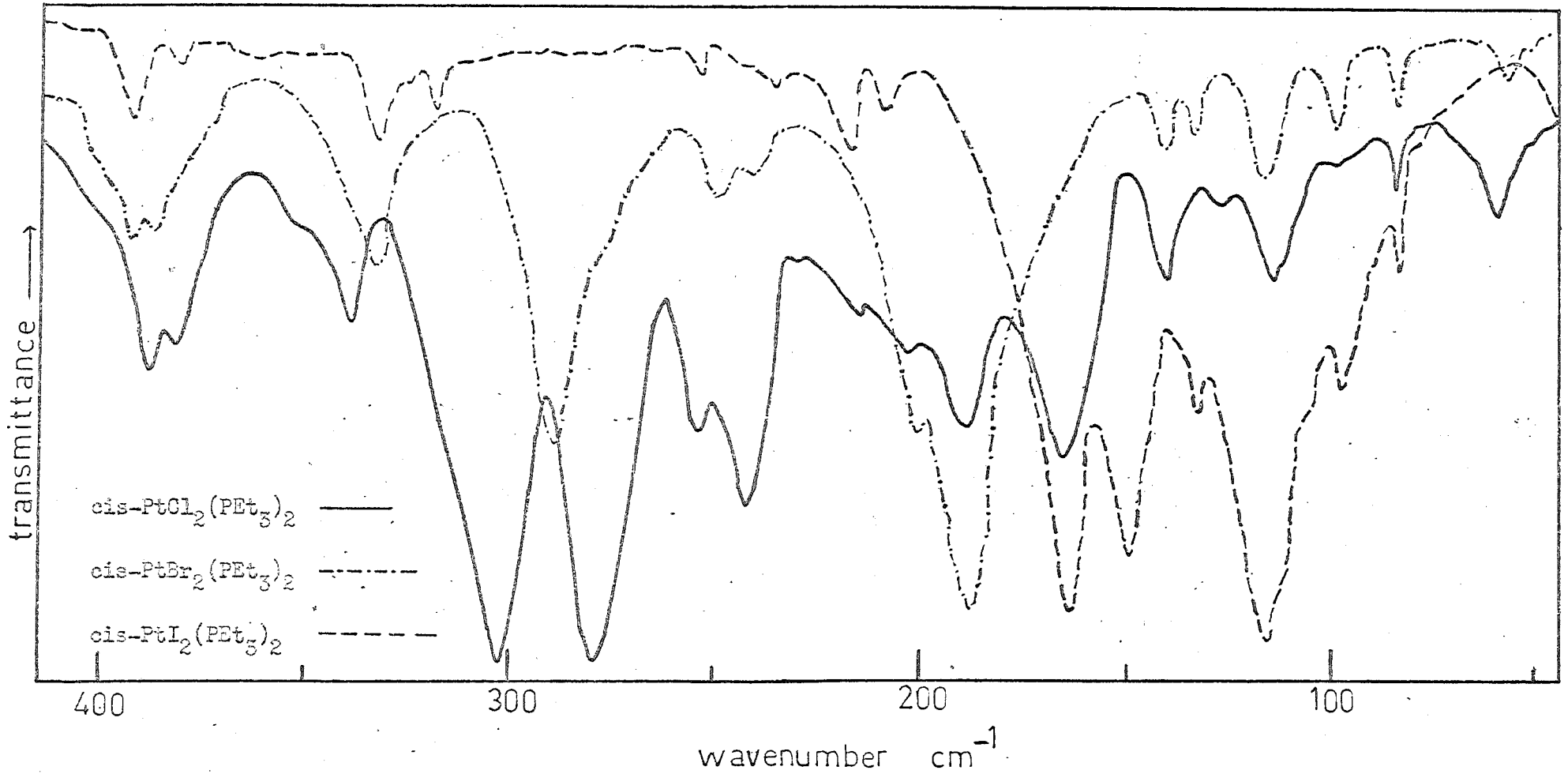
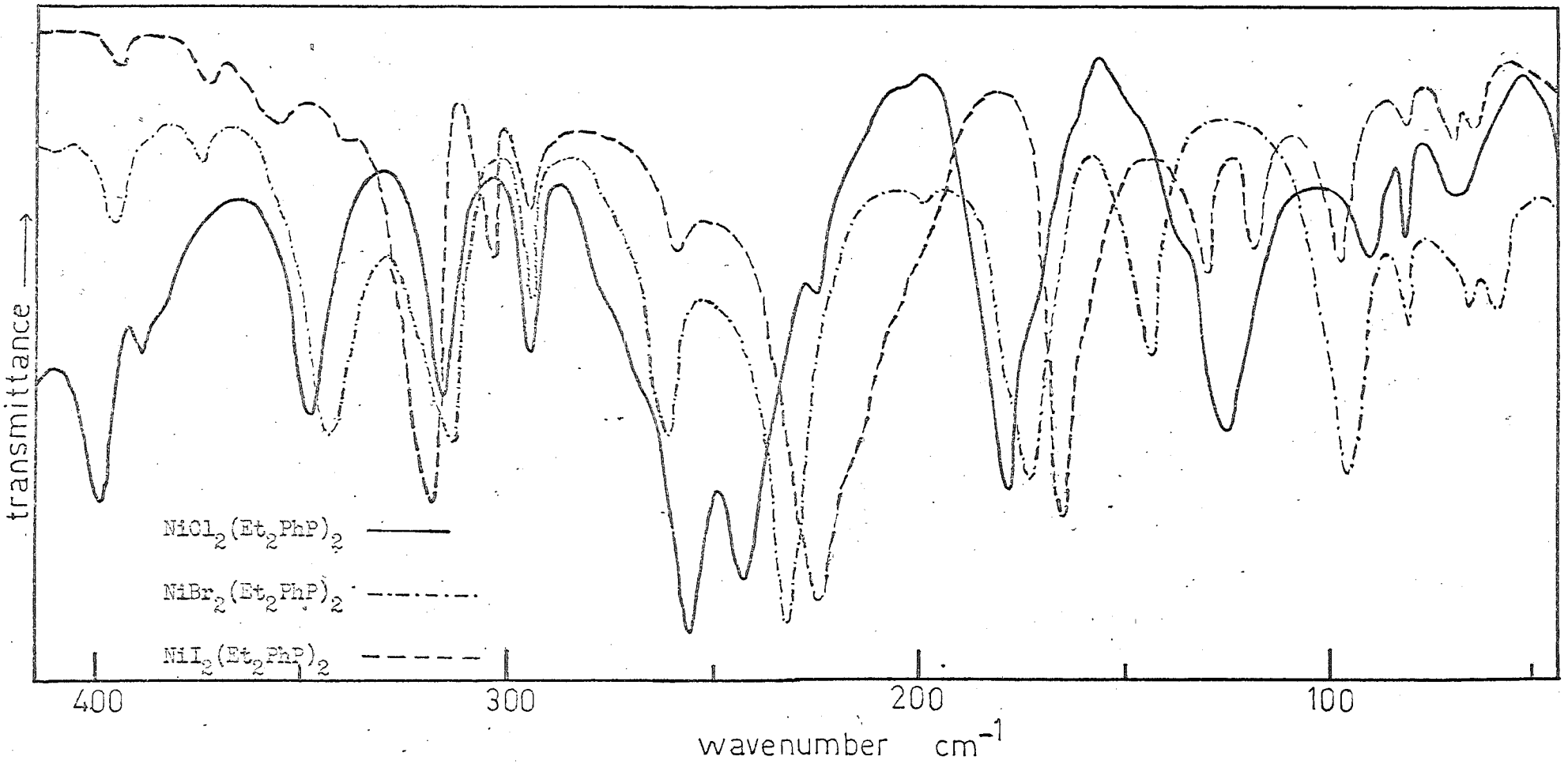


FIGURE 2·3

FAR INFRA-RED SPECTRA OF NICKEL(II) COMPLEXES OF Et_2PhP



and previous workers[68,69] have not assigned specific descriptions to the three in-plane and one out-of-plane bending modes expected from theory because of the probability of mixing of these vibrations.

In the present work the cis complexes studied are mostly those of platinum (II), However, depending on the nature of the tertiary phosphine ligand, cis complexes of palladium can be isolated, and the separation of the cis and trans isomers of $PdCl_2(Et_2PhP)_2$ has been achieved in this work (see Experimental section, p. 77).

(i) Metal-halogen stretching vibrations:- The two expected infra-red active metal-halogen stretching vibrations in these cis complexes have A_1 and B_1 symmetry (symmetric and asymmetric stretching respectively). The spectra have been assigned by comparison of complexes differing only in halogen, and Tables 2.5 and 2.6 contain these assignments. In the case of cis - $PtBr_2(PEt_3)_2$ the absorption at higher energy (201 cm^{-1}) occurs as a shoulder on the more intense and broader absorption centred at 188 cm^{-1}. These have been assigned to the symmetric and asymmetric ν(M-X) vibrations respectively. The frequencies of these two absorptions agree well with the data of Goggin et al.[69], but are in conflict with the assignments of Adams et al.[68], who select 211 cm^{-1} as the higher-lying of the two Pt-Br vibrations. Goggin et al.[69] have noted that Raman studies show that the higher-lying of the two absorptions corresponds to the symmetric stretching vibration (A_1 symmetry). These workers also report that in the infra-red the symmetric stretch gives rise to the least intense and the asymmetric stretch to the most intense absorption. This intensity relationship is found in the present work in most cases; in some compounds the symmetric

and asymmetric modes are of approximately equal intensity (see Tables 2.5 and 2.6).

Partial assignment of the low frequency infra-red spectrum of cis - $PdCl_2(Et_2PhP)_2$ (Table 2.6) has been made. The ν(Pd-Cl) modes are assigned on the basis of their strong intensity. This work on cis - $PdCl_2(Et_2PhP)_2$ was carried out independently of a more extensive study of cis - palladium (II) phosphine complexes by Allen and Wilkinson which has recently appeared in the literature.[103] The metal - halogen vibrations of cis - $PdCl_2(Et_2PhP)_2$ were assigned by these workers to bands at 305 cm^{-1} and 290 cm^{-1}. The assignments of the present work (308 cm^{-1} and 292 cm^{-1}) are therefore in agreement with these.

(ii) Metal-phosphorus stretching vibrations:- As in the case of the metal-halogen vibrations two infra-red active metal-phosphorus stretching vibrations are expected for the cis complexes. These vibrations have A_1 symmetry (symmetric stretch) and B_1 symmetry (asymmetric stretch). It is likely that previous assignments[68,69] of ν_a(M-P) and ν_s(M-P) for these complexes are again in error, by analogy with the situation discussed above for the trans complexes. However there is some difficulty in making unambiguous assignments of ν(M-P) in these spectra for several reasons.

It is not altogether certain to what extent the metal-phosphorus bond strength will be greater in the cis complexes as compared with the trans analogues, though that it is greater has been shown by Chatt and Wilkins[30,31] from thermodynamic studies on cis and trans $PtCl_2(PEt_3)_2$ complexes. On this basis the frequencies of ν(M-P) stretching vibrations in cis complexes should be higher than in the trans analogues. However steric effects also need to be taken into account. From a consideration

of molecular models it can be shown that there is considerable intramolecular interaction in the cis complexes and this is confirmed by comparison of single crystal X-ray structures for cis and trans complexes. For example the crystal structures of the isomorphous pair, trans - $PtCl_2(PEt_3)_2$ and trans - $PtBr_2(PEt_3)_2$[65] show that the P_2PtX_2 grouping is planar while for the complex cis - $PtCl_2(PMe_3)_2$,[37] the PtP_2Cl_2 grouping is somewhat distorted from planarity towards a tetrahedral configuration, with the P-Pt-P′ angle = 96.3°. It would be expected that this distortion will be even more severe for the bromo and iodo complexes. Thus to describe the cis complexes in terms of C_{2v} symmetry is more formal than real and the lowered symmetry is likely to influence the vibrational spectra. Both coupling of vibrational modes and general steric pressure imposed by the phosphine ligands in cis complexes are likely to modify the positions of the metal-phosphorus vibrations in particular.

The tentative assignments made for ν(M-P) in the present work are given in Tables 2.5 and 2.6. For cis - $PtBr_2(PEt_3)_2$ the medium strong absorption at 285 cm^{-1} is assigned to ν_s(M-P) but the second metal-phosphorus vibration, ν_a(M-P), cannot be located. In contrast, for the Et_2PhP bromo complex only the ν_a(M-P) vibration can be satisfactorily assigned (228 cm^{-1}). The platinum chloro complexes for both Et_2PhP and PEt_3 as phosphines show two weak or medium bands in the 260 cm^{-1} and 220 cm^{-1} regions, corresponding to ν_s(M-P) and ν_a(M-P) respectively. The intensities of these absorptions are in agreement with the intensity relationship noted by Goggin et al.[69] for the metal-halogen stretching modes (see above).

The platinum iodo complex with PEt_3 as ligand has an

TABLE 2.7

Infra-red active normal modes of vibration for binuclear halogen-bridged $M_2X_4L_2$ complexes[85]

Symmetry	Approximate Description	Number Expected
b_u	terminal M-X stretching, $\nu_a(M\text{-}X)_t$	1
b_u	bridging M-X stretching, $\nu_a(M\text{-}X)_b$	2
b_u	metal-phosphorus stretching, $\nu_a(M\text{-}P)$	1
b_u	terminal M-X bending, in-plane, $\delta(M\text{-}X)$	1
b_u	metal-phosphorus bending, in-plane, $\delta(M\text{-}P)$	1
a_u	out-of-plane bridge bending, $\pi(M_2X_2)$	1
a_u	terminal M-X bending, out-of-plane, $\pi(M\text{-}X)$	1
a_u	metal-phosphorus bending, out-of-plane, $\pi(M\text{-}P)$	1

infra-red spectrum which is devoid of absorption in the 250-300 cm^{-1} region where ν_s(M-P) might be expected to occur. For the Et_2PhP analogue however both metal-phosphorus vibrations can be satisfactorily assigned.

The cis - palladium complex, cis - $PdCl_2(Et_2PhP)_2$, shows absorptions assignable to ν(Pd-P) at 257 cm^{-1} (ν_s(Pd-P)) and 222 cm^{-1} (ν_a(Pd-P)) respectively. The lower-lying of this pair was assigned to ν(Pd-P) by Allen and Wilkinson.[103] These workers however made no assignment for the other expected metal-phosphorus stretching vibration.

(iii) In-plane and out-of-plane bending modes:- As noted above it is not realistic to make specific assignments of the three in-plane and one out-of-plane bending modes expected from theoretical considerations, since mixing of these vibrations is probable in the cis complexes.[68,69,104] Tables 2.5 and 2.6 contain the absorptions assigned in the present work to bending modes.

(d) Infra-red assignments of metal-ligand vibrations for binuclear halogen-bridged complexes:-

The structure of halogen-bridged binuclear complexes of palladium (II) and platinum (II) has been discussed earlier in this thesis (p. 18). These complexes of general formula $M_2X_4L_2$, where M = Pd or Pt ; X = Cl, Br or I; and L = PEt_3 in the present work, belong to the point group C_{2h}, if PEt_3 is treated as a point mass. The infra-red active normal modes of vibration expected for these complexes[85] are shown in Table 2.7, and assignments have been made as follows.

(i) Terminal metal-halogen stretching vibration:- The one expected infra-red active metal-halogen asymmetric stretching vibration (b_u symmetry) involving the terminal halogeno ligands

TABLE 2.8

Far Infra-Red Spectra : Assignments for binuclear halogen-bridged triethylphosphine complexes

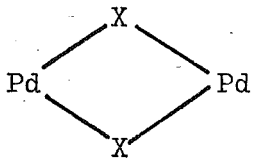
frequencies in cm^{-1}

BAND ASSIGNMENT	$Pd_2Cl_4(PEt_3)_2$	$Pd_2Br_4(PEt_3)_2$	$Pd_2I_4(PEt_3)_2$	$Pt_2Cl_4(PEt_3)_2$	$Pt_2Br_4(PEt_3)_2$	$Pt_2I_4(PEt_3)_2$
ν_a(M-X) terminal	356m	267m	236w	350ms 344m,sh	246m	207wm
ν_a(M-X) bridging trans to X	303wm	195ms	165m,sh	327m 320m,sh	210m	168m,sh
ν_a(M-X) bridging trans to P	260m	166m	140w	265s,br	185s	146m
ν_a(M-P)	248m	251wm	252wm	255m,sh	(a)	247m
Bending Modes	154s 120vw			140m 123w	159wm 140w	125wm 110m
δ(MPC)	177m,sh	185s	171s	183m	(a)	175s
δ(CCP)	377w 329w	371w 323w 290w	372wm 333wm 212w	385w	387w,sh 363w 330m 267w	381m 366w 335m 267w
π(MPC)	93w,br	110m,br	106w,vbr	95w,br	105m,br	95w,br
LATTICE	46w	(b)	57w	45w	60w	50m

(a) masked

(b) no absorption assignable

has been readily assigned in the present work (Table 2.8) on the basis of intensity (apart from iodides) and also its close similarity in energy to the asymmetric metal-halogen stretching vibration for trans mononuclear species (Table 2.2). The only difficult assignment is for $Pd_2I_4(PEt_3)_2$. The infra-red spectrum of this complex contains two weak absorptions in the expected region, one at 212 cm^{-1} and the other at 236 cm^{-1}. The latter seems a little high, since ν_a(Pd-I) for trans-$PdI_2(PEt_3)_2$ is observed at 218 cm^{-1} (Table 2.2). However, Adams and Chandler[85] consider that the grouping



may not be planar in the binuclear iodo compound and this would invalidate the correlation with the mononuclear trans complexes which is possible for $\nu_a(M\text{-}X)_t$ in the chloro and bromo complexes.

(ii) Bridging metal-halogen stretching vibrations:- There are two infra-red active metal-halogen asymmetric stretching vibrations for the halogen bridge system. These both have b_u symmetry, with the higher-lying mode being assigned to $\nu_a(M\text{-}X)_b$ trans to a terminal halogen and the lower-lying mode to $\nu_a(M\text{-}X)_b$ trans to the phosphine ligand.[85] The assignments made in the present work are given in Table 2.8. These assignments agree in the main with those of Goggin et al.[69] The principal difference occurs in the 180 $\pm$ 10 cm^{-1} region where the in-plane metal-phosphorus-carbon bending vibration occurs as a strong absorption in all cases (Table 2.8). Therefore, it is more realistic in the case of $Pd_2Br_4(PEt_3)_2$ to assign the medium intensity absorption at 166 cm^{-1} to ν_a(Pd-Br) bridging trans to the phosphine ligand, and the strong band at 185 cm^{-1} to the bending mode, δ (PdPC). For the iodo-bridged complexes of both palladium and platinum a similar situation exists and again it

is considered unlikely that Pd-I and Pt-I bridging vibrations will have the strong intensity of the 171 cm^{-1} and 175 cm^{-1} absorptions respectively. These are thus assigned to δ (PdPC) and δ (PtPC).

(iii) Metal-phosphorus stretching vibration:- The one expected infra-red active metal-phosphorus asymmetric stretching vibration (b_u symmetry) has been assigned by comparison with ν_a (M-P) for analogous cis mononuclear complexes, and after assignment of the various metal-halogen modes. It seems likely by analogy with the situation for mononuclear trans complexes that previous assignments[69,85] of ν_a(M-P) in the 400-450 cm^{-1} region in these complexes are in error. Thus the revised assignments of Table 2.8 have been made.

For the complex $Pt_2Br_4(PEt_3)_2$ no satisfactory assignment of ν_a (Pt-P) can be made since the terminal platinum-bromine stretching vibration occurs in the expected region of the platinum-phosphorus mode (250 cm^{-1}), and is likely to be the more intense, hence masking ν_a (Pt-P).

(iv) In-plane and out-of-plane bending modes:- In-plane and out-of-plane bending modes of the forms given in Table 2.7 are expected to occur in the lower energy region of these spectra. Up to five such absorptions are expected from theory but in the present work only two of these bending modes have been located. As for the cis mononuclear complexes discussed previously there is a likelihood of some mixing of modes of the same symmetry since these are expected to be close to each other in energy in the lower frequency region of the spectrum. The absorptions assigned as bending modes in Table 2.8 are therefore not differentiated as to their possible characteristics.

Trends in the far infra-red spectra of square planar complexes.

(i) δ (MPC) vibrations: As can be seen from the tabulated frequencies (Tables 2.2 - 2.12) each group of complexes shows a decrease in the frequency of the in-plane metal-phosphorus-carbon bending mode with change in halogen from chlorine to bromine to iodine. There are two possible explanations for this; the first is that it is a steric effect reflecting the increase in halogen size in the above order, and hence an increase in non-bonded intereactions between halogen and the ethyl groups of the phosphine ligands. The second explanation is that the decrease in frequency reflects an increasing withdrawal of electron density from the phosphine ligand with change in halogen in the above order. This increasing charge draw-off could arise through $M_{d\pi} \rightarrow X_{d\pi}$ bonding between metal and halogen, with available halogen d orbitals for such bonding increasing in the order $Cl < Br < I$, as discussed previously in Chapter 1. The effect of metal to halogen π bonding is to increase the positive charge on the metal ion and this would increase the attraction of the metal ion for charge from the other ligands. Hence charge draw-off from the phosphine ligands might be expected on this basis, leading to a lowering of frequency for the metal-phosphorus-carbon bending mode, as is observed. The increasing polarizability of the halogeno ligands in the order $Cl < Br < I$ (Chapter 1) would probably result in a similar effect since the more polarizable halogens will induce a greater positive charge on the metal ion and hence a similar charge draw-off to that discussed above in terms of $M_{d\pi} \rightarrow X_{d\pi}$ bonding might be expected to occur. It is probable that no one of the above explanations dominates over the others, and that all possibilities play some part in the

overall situation.

Another trend of interest concerns the relative intensities of the δ (MPC) vibration in trans mononuclear complexes as compared with cis isomers. It is clear from the tables of frequencies that, in general, the δ (MPC) vibration in trans complexes is more intense than for the cis analogues. The selection rule governing absorption of infra-red energy is related to a change in dipole moment for a vibration to be infra-red active. Further, the maximum change in dipole moment will produce the maximum intensity for an infra-red active vibration, as measured by the transition moment.[105] It can be recalled from previous discussion (p. 29) that molecular models make it clear that intramolecular interactions are greater in cis complexes as compared with trans complexes. Thus it may be that the lower intensity for the δ (MPC) vibrational absorption in cis complexes reflects these intramolecular interactions which do not allow a maximum change in dipole moment to be exercised by the vibration.

(II) ν(M-P) vibrations:- The asymmetric metal-phosphorus stretching vibration in trans mononuclear complexes shows a general decrease in frequency with change in halogen from chlorine to bromine to iodine. Tentatively, this might be ascribed to competition for suitable π -bonding orbitals between the halogeno and phosphine ligands. The ability of the halogens to form $M_{d\pi} - X_{d\pi}$ bonds is expected to increase in the order Cl < Br < I (see Chapter 1) and hence the competition for metal π orbitals noted above will be greatest in iodo complexes. This may therefore account for the decrease of ν_a(M-P) with change in halogen in the above order. If the above explanation is correct then the effect on the metal-phosphorus bond in cis

TABLE 2.9

Asymmetric metal-halogen stretching frequencies for trans-square planar complexes

frequencies in cm^{-1}

X	$NiX_2(PEt_3)_2$	$NiX_2(Et_2PhP)_2$	$PdX_2(PEt_3)_2$	$PdX_2(Et_2PhP)_2$	$PtX_2(PEt_3)_2$
Cl	403	398	356	353	340
Br	338	336	269	270	252
I	307	302	218	212	201

TABLE 2.10

Stretching force constants of metal-halogen bonds in trans-square planar complexes

force constants in $(N.m^{-1})x10^2$

X	$NiX_2(PEt_3)_2$	$NiX_2(Et_2PhP)_2$	$PdX_2(PEt_3)_2$	$PdX_2(Et_2PhP)_2$	$PtX_2(PEt_3)_2$
Cl	2.12	2.10	1.99	1.95	2.04
Br	2.28	2.25	1.94	1.96	2.12
I	2.23	2.16	1.62	1.53	1.83

complexes should be greater. However, the ν(M-P) modes for cis mononuclear compounds are likely to be affected by coupling interactions with metal-halogen stretching modes of the same symmetry (see earlier discussion, pp. 26,27) and since the degree of this interaction is uncertain it is not reasonable to undertake an extensive discussion.

(iii) ν(M-X) vibrations:- For metal-halogen stretching vibrations the analysis of trends in the spectra is more difficult. Crude stretching force constants for metal-halogen bonds in the trans mononuclear complexes have been calculated in the present work using the equation $\nu = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}}$, where the symbols have their usual meanings, and employing the experimentally measured values of ν_a (M-X) for the trans complexes (Table 2.9). The force constants calculated by this method are given in Table 2.10. Although these parameters do not take into account possible coupling interactions for ν_a (M-X) this may not be a serious problem in trans mononuclear complexes.

The high values of the force constants calculated for nickel complexes are not expected on the basis of the relative instability of the complexes and this may be taken as emphasising the approximations inherent in the calculations.

There is a small but consistent increase in force constants between analogous complexes of palladium and platinum. A tentative explanation for this is that the π-bonding ability of platinum should be greater than that of palladium, thus leading to a greater $M_{d\pi} - X_{d\pi}$ bonding interaction with the halogeno ligands.

Low frequency infra-red spectra of tetrahedral cobalt (II) complexes:-

The cobalt (II) complexes studied in this work have general formula CoX_2L_2, where X = Cl, Br or I and L = PEt_3. The

TABLE 2.11

Infra-red active normal modes of vibration for tetrahedral MX_2L_2 complexes.[106]

Symmetry	Approximate Description	Number expected
A_1	symmetric M-X stretching	1
A_1	symmetric M-P stretching	1
B_1	asymmetric M-X stretching	1
B_2	asymmetric M-P stretching	1
	MX_2 and MP_2 in and out-of-plane bending (see text)	5

TABLE 2.12

Far Infra-Red Spectra : Assignments for tetrahedral cobalt complexes

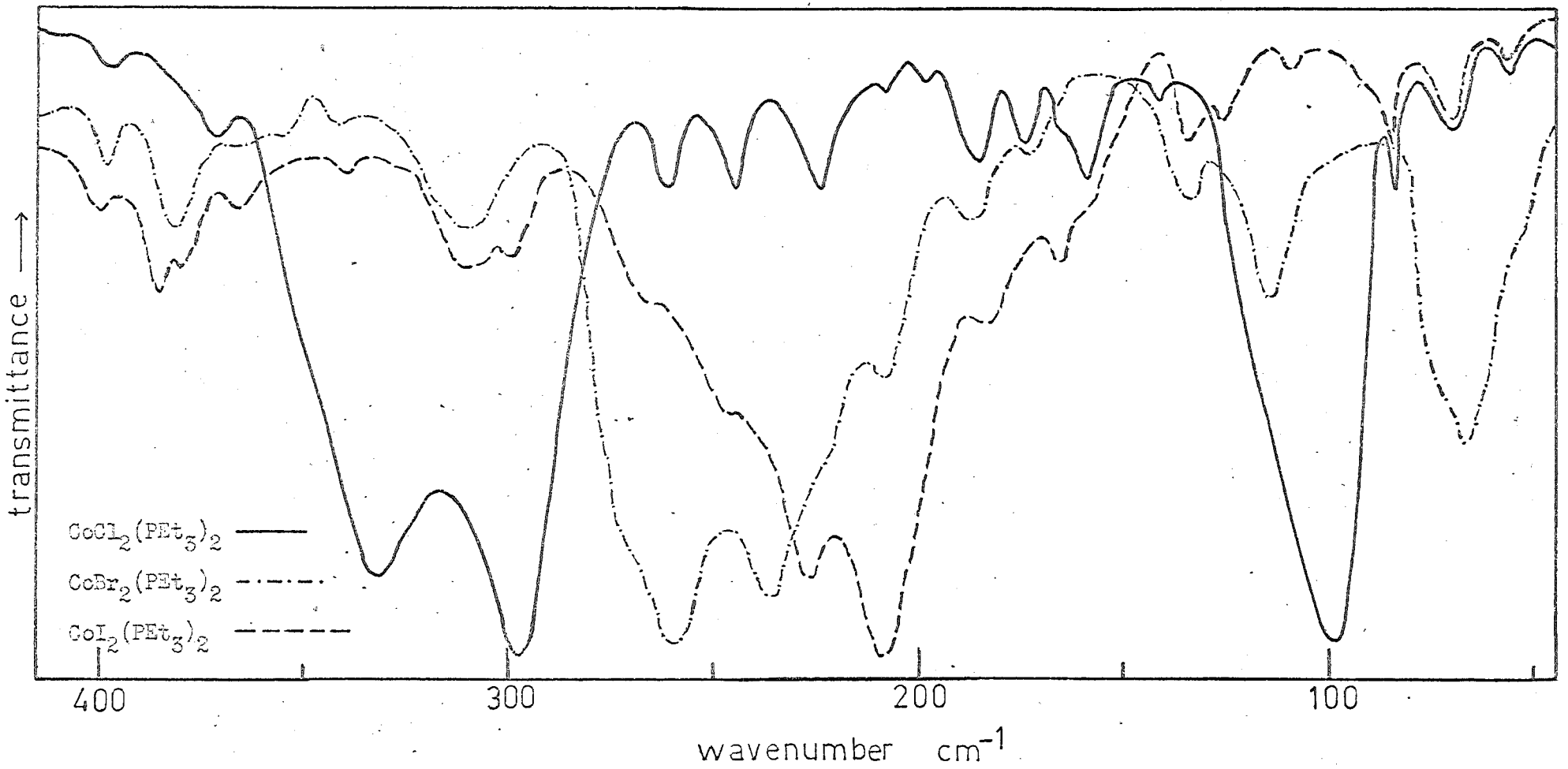
frequencies in cm^{-1}

BAND ASSIGNMENT	$CoCl_2(PEt_3)_2$	$CoBr_2(PEt_3)_2$	$CoI_2(PEt_3)_2$	$CoBr_2(Et_2PhP)_2$
ν_a(M-X)	333s	260s	212s	268s
ν_s(M-X)	298s	241s	192m	241s
ν_a(M-P)	245w	(a)	252w	215m
ν_s(M-P)	226wm	225sh	225m	202w
Bending Modes	170w	144w	152w	167w
	156w	123w	121w	140w
		103w		90w
δ(MPC)	186w	180w	170w	175w
δ(CCP)	382w	370wm	378w	
	362w			
	263w	318w	301w	312w
	202w	202w		195wm
LATTICE	102ms,br	70m,br		77m
	57w		58wm	65w

(a) masked

FIGURE 2·4

FAR INFRA-RED SPECTRA OF TETRAHEDRAL COBALT(II) COMPLEXES



only complex of Et_2PhP which could be obtained in a satisfactory crystalline form was $CoBr_2(Et_2PhP)_2$. The complexes have a tetrahedral arrangement of ligands (p. 18), and the symmetry will be C_{2v} if the complexes are regular tetrahedral. The form and symmetry of the normal modes of vibration[106] for CoX_2L_2 complexes are given in Table 2.11. As discussed previously for cis square planar complexes (p. 27) considerable mixing of the five predicted skeletal bending modes is probable, and hence in previous infra-red studies of tetrahedral cobalt (II) complexes[94,106] no attempt has been made to assign absorptions arising from bending vibrations to any particular bending mode. The spectra obtained in the present work are listed in Table 2.12 and represented diagrammatically in Figure 2.4.

Assignment of Spectra:-

The infra-red spectra of the complexes with triethylphosphine as ligand have not been discussed previously. Bradbury et al.[94] have assigned the metal-halogen and metal-phosphorus stretching modes in $CoX_2(Ph_3P)_2$ complexes and Clark and Williams[106,107] have discussed pyridine complexes of cobalt (II). The assignments of metal-halogen stretching vibrations in the present work are similar to those made for the pyridine and Ph_3P complexes.

The Co-X stretching vibrations give rise to intense, broad absorptions (half-band width 40 cm^{-1}). Assignments have been made on the basis of intensity and also by comparison of complexes differing only in halogen. The metal-phosphorus stretching vibrations are of medium intensity and, in general, the two expected bands can be assigned in the 220-260 cm^{-1} region, except where this region is dominated by intense ν(Co-X) absorptions, as in $CoBr_2(PEt_3)_2$. A number of very weak absorptions

TABLE 2.13

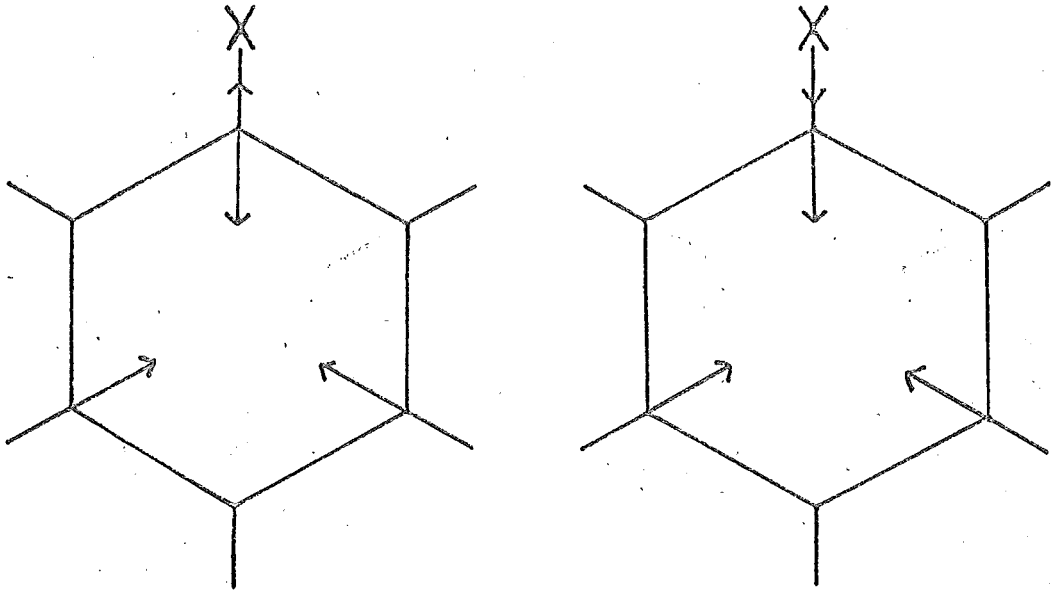
X-mode frequencies (cm^{-1}) for some $MX_2(Et_2PhP)_2$ complexes

	X-mode designation (after Whiffen[108])			
Compound	q	r	u	x
Et_2PhP	1092	682	285	185
$NiCl_2(Et_2PhP)_2$	1098	702	292	193
$NiBr_2(Et_2PhP)_2$	1108	702	290	195
$NiI_2(Et_2PhP)_2$	1100	702	290	192
$PdCl_2(Et_2PhP)_2$	1098	709	295	(a)
$PdBr_2(Et_2PhP)_2$	1105	703	298	(a)
$PdI_2(Et_2PhP)_2$	1100	704	294	(a)
cis-$PtCl_2(Et_2PhP)_2$	1099	710	289	192
cis-$PtBr_2(Et_2PhP)_2$	1108	710	291	188
cis-$PtI_2(Et_2PhP)_2$	1102	708	295	(a)

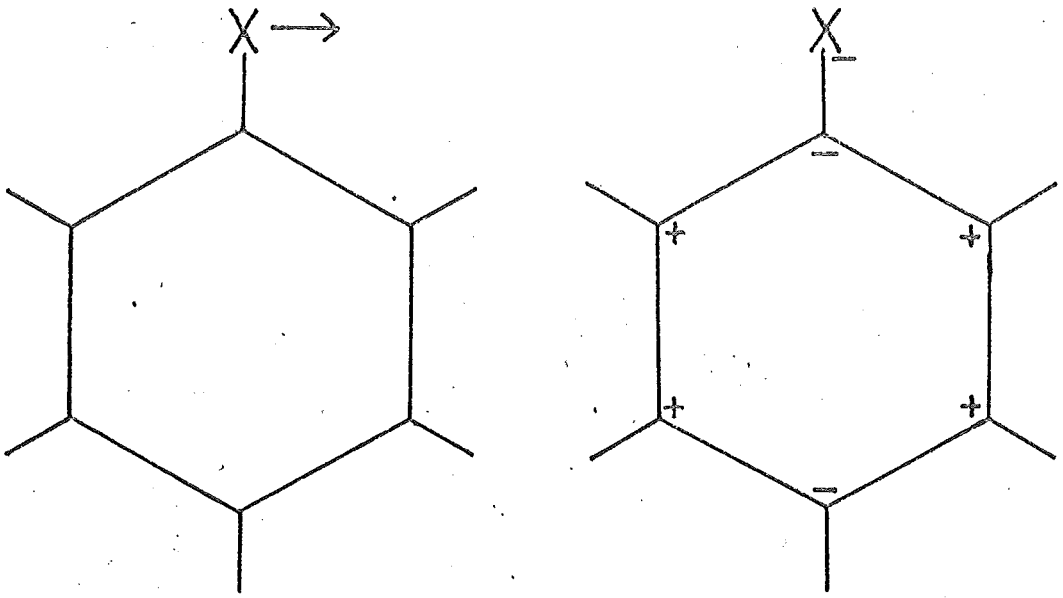
(a) masked

FIGURE 2·5

DIAGRAMMATIC REPRESENTATION OF WHIFFEN "X-MODES" (see text)



q mode r mode



u mode x mode

in the 100-200 cm^{-1} region may be assigned to bending modes, although their character cannot be assigned. A weak band at 180 cm^{-1} may be attributable to the cobalt-phosphorus-carbon bending mode, δ (CoPC).

In the very low energy region of the spectra of PEt_3 complexes a rather intense absorption occurs. In the chloro complex the band is found at 102 cm^{-1} with a half-band width of 20 cm^{-1}. For the bromo complex the band is somewhat less intense and occurs at 70 cm^{-1} with a half-band width of 35 cm^{-1}. However for $CoI_2(PEt_3)_2$ it appears that the change in halogen has lowered the energy of the vibration below 40 cm^{-1}, the limit of measurement in this work. It is possible that the absorption corresponds to a lattice vibration which is influenced by the halogeno ligands.

X-sensitive vibrations:-

The diethylphenylphosphine complexes studied in this work exhibit a number of vibrations involving the phenyl ring which are said to be "X-sensitive". These modes arise from vibrations involving the aromatic ring and the atom to which it is bound, in this case a phosphorus atom. This is analogous to a halobenzene system, and these were the subject of the original vibrational study by Whiffen.[108] These vibrations should be sensitive to the electronic requirements of the phosphorus atom,[100,109,110] and hence the frequencies of infra-red absorptions could be modified by changes in halogeno ligand.

The tabulated data for the complexes studied in the present work show certain consistent trends (see Table 2.13) but these changes are too small to be significant since the uncertainties in measurement are relatively large ($\pm$ 5 cm^{-1} in the high frequency, and $\pm$ 2 cm^{-1} in the low frequency region). Table 2.13

FIGURE 2·6

^{1}H NMR SPECTRA OF PHOSPHINE LIGANDS

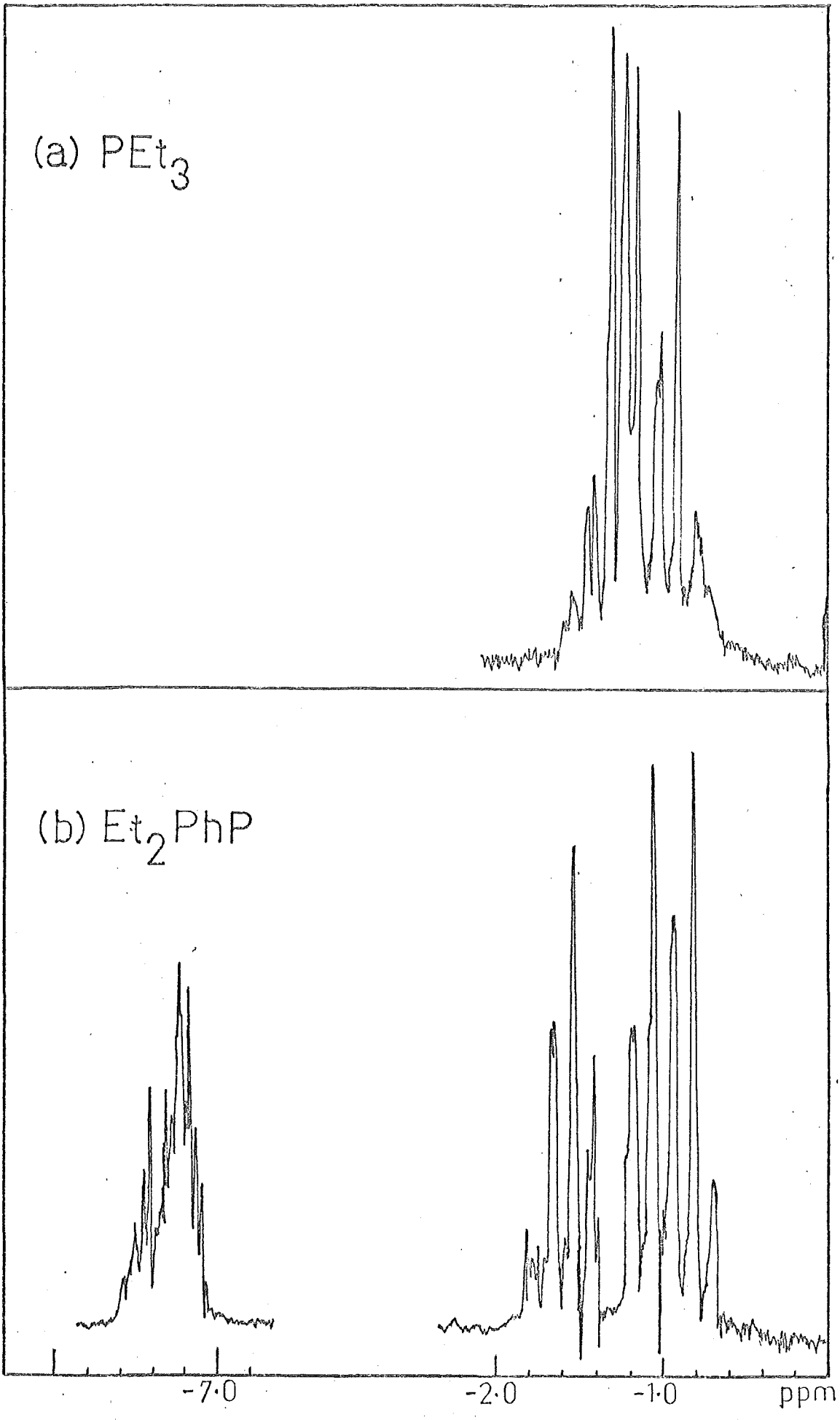


FIGURE 2·6 cont'd

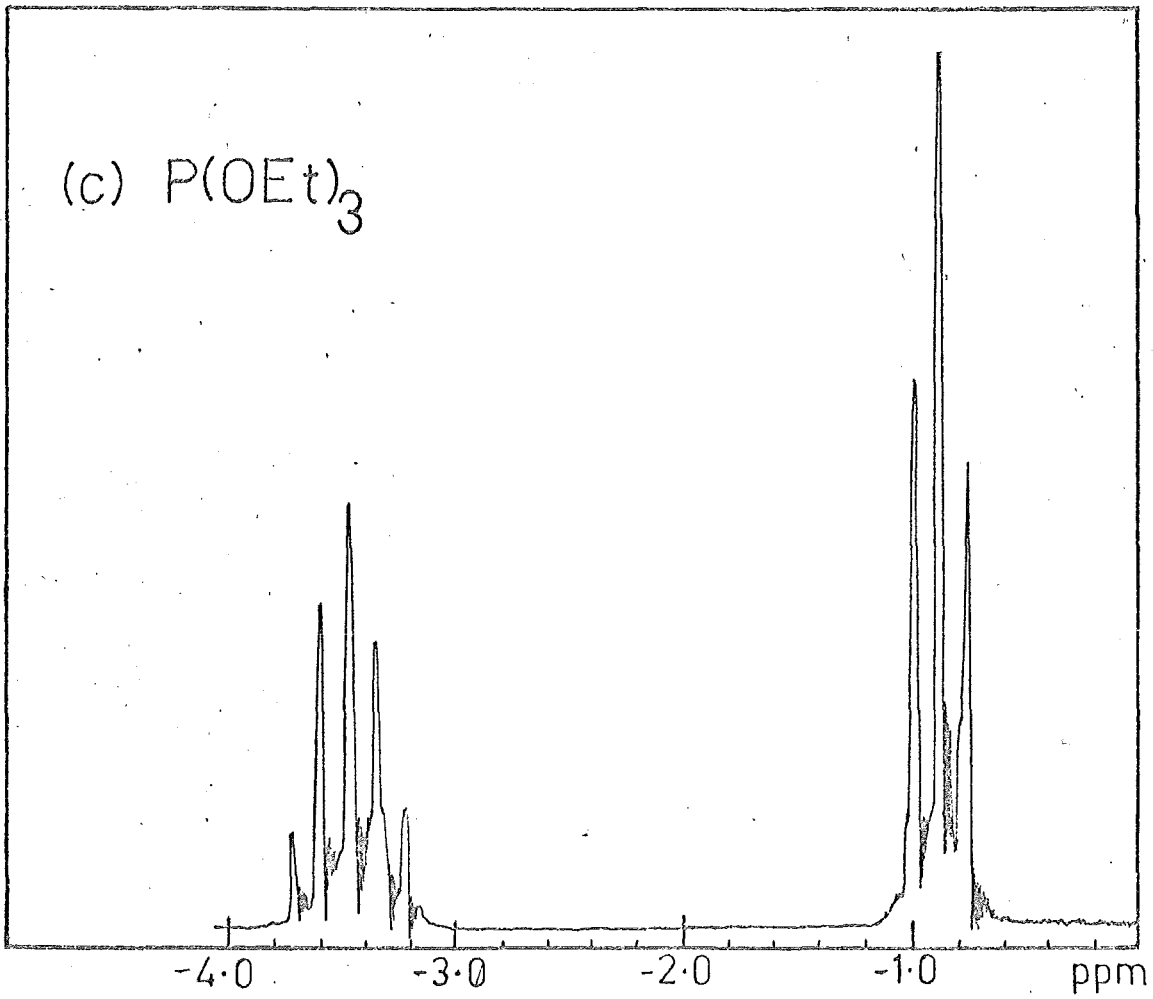
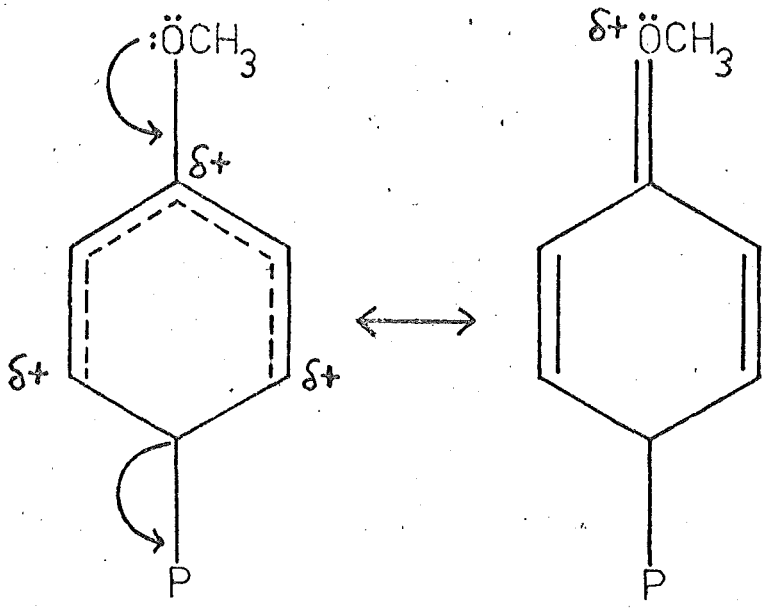


FIGURE 2·13

MESOMERIC ELECTRON DONATION BY A PARA METHOXY SUBSTITUENT



gives the measured frequencies of the q, r, u and x modes observed in this work and Fig. 2.5 shows diagrammatically the types of vibration which give rise to these absorptions, using the terminology of Whiffen.[108]

2.2.2 Proton Magnetic Resonance Spectra

Introduction:-

The ^{1}H NMR spectra of the four-coordinate complexes have been recorded in deuteriochloroform solution. The spectra contain up to three main regions of absorption arising from the resonances of methyl, methylene and, for diethylphenylphosphine, phenyl protons. These resonances occur in the general regions -1.0, -2.0 and -7.5 ppm respectively, relative to TMS as zero, but show significant variations with change in metal, and particularly with change in the halogeno ligand.

^{1}H NMR spectra of the free ligands:-

Rogers and Narasimhan[111] have discussed the ^{1}H NMR spectrum of triethylphosphine in some detail and have shown how it can be calculated from a theoretical standpoint assuming an $A_3A_2'X$ spin system and various required coupling constants. The spectrum obtained in the present work (Figure 2.6(a)) agrees well with the results of Rogers and Narasimhan.[111] Thus $^{2}J(^{31}P-^{1}H)$ = 14Hz (13.7Hz [111]) and $^{1}J(^{31}P-^{1}H)$ is too small to be resolved (0.5Hz [111]).

The ^{1}H NMR spectrum of diethylphenylphosphine has been discussed by Randall and Shaw.[112] In the present work the value of $^{2}J(^{31}P-^{1}H)$ for the doublet splitting of the two overlapping methyl triplets is found to be 14Hz (13.8Hz [112]), and again the value of $^{1}J(^{31}P-^{1}H)$ is too small to be resolved (0.5Hz [112]). The multiplet arising from the phenyl protons is rather complex.

FIGURE 2·9

^{1}H NMR SPECTRA OF CIS-PLATINUM(II) COMPLEXES

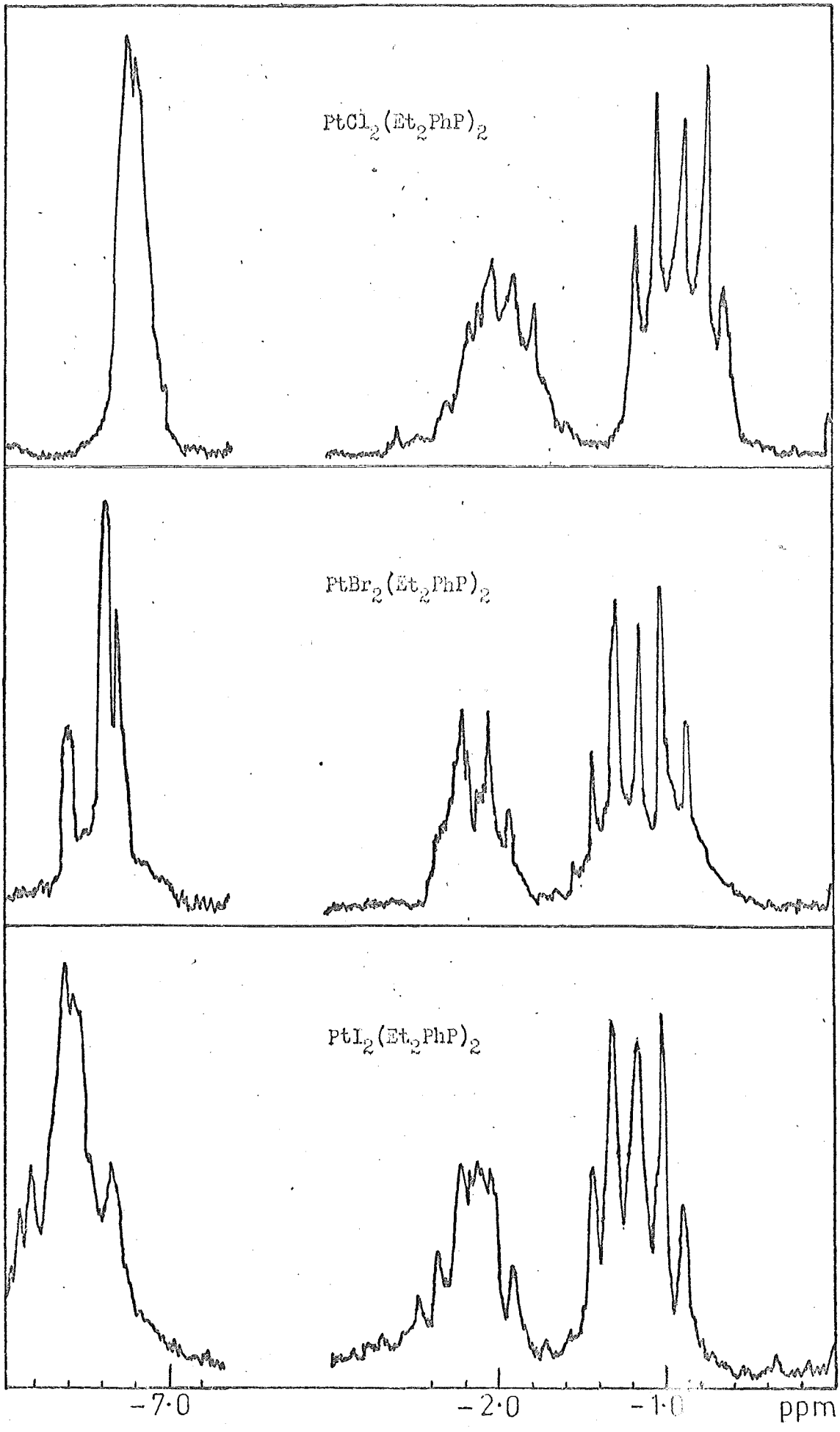
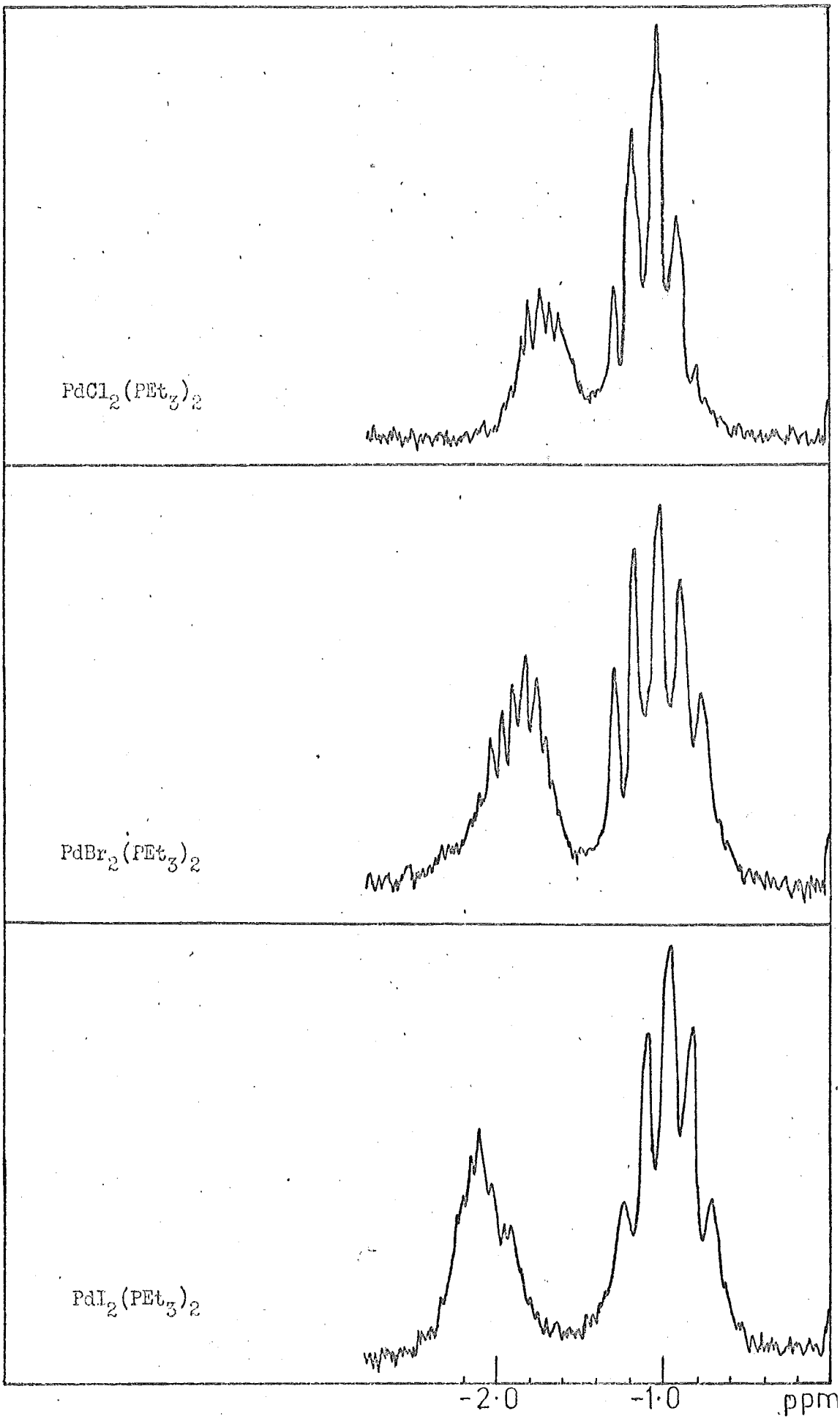


FIGURE 2·10

^{1}H NMR SPECTRA OF TRANS PALLADIUM(II) COMPLEXES



However it is of some interest that the ortho protons are very slightly deshielded relative to the rest of the multiplet (Figure 2.6(b)).

The spectrum of triethylphosphite is rather simple. The 1:2:1 triplet for the methyl multiplet shows no evidence of coupling with the phosphorus nucleus. However the 1:3:4:3:1 quintet for the methylene protons arises from the overlap of two 1:2:2:1 quartets with $^{1}J(^{31}P\_^{1}H) = 7Hz$. The spectrum is reproduced in Figure 2.6(c).

^{1}H NMR spectra of square planar complexes

(a) Analysis of the methyl and methylene multiplets:-

For an ethyl group for which no complications occur (e.g. ethyl in ethylbenzene) the methyl resonance occurs as a 1:2:1 triplet and the methylene resonance as a 1:2:2:1 quartet, these ratios arising naturally from proton-proton coupling. For the cis phosphine complexes studied in the present work the effect of the phosphorus nucleus (spin $\frac{1}{2}$) should be to further split the triplet of the methyl group into two triplets which will overlap in a manner dependent upon the magnitude of the phosphorus-proton coupling constant. Thus the spectra shown in Fig. 2.9 have a five line (1:2:2:2:1) multiplet for the methyl resonance arising from overlap of two triplets, with $^{2}J(^{31}P\_^{1}H)$ approximately 19Hz . There is no observable variation in this coupling constant with change in halogen. A reasonable spectrum of the only non-platinum cis complex, cis- $PdCl_2(Et_2PhP)_2$, could not be obtained because of rapid isomerization in solution. In the ^{1}H NMR spectrum the complex mixture of resonances arising from cis and trans isomers of the equilibrium mixture could not be separated into the component resonances. The simpler ^{13}C NMR spectrum could however be resolved into cis and trans components (see later discussion).

FIGURE 2·11

MULTIPLICITY OF METHYL RESONANCES IN ^{1}H NMR SPECTRA OF CIS AND TRANS COMPLEXES

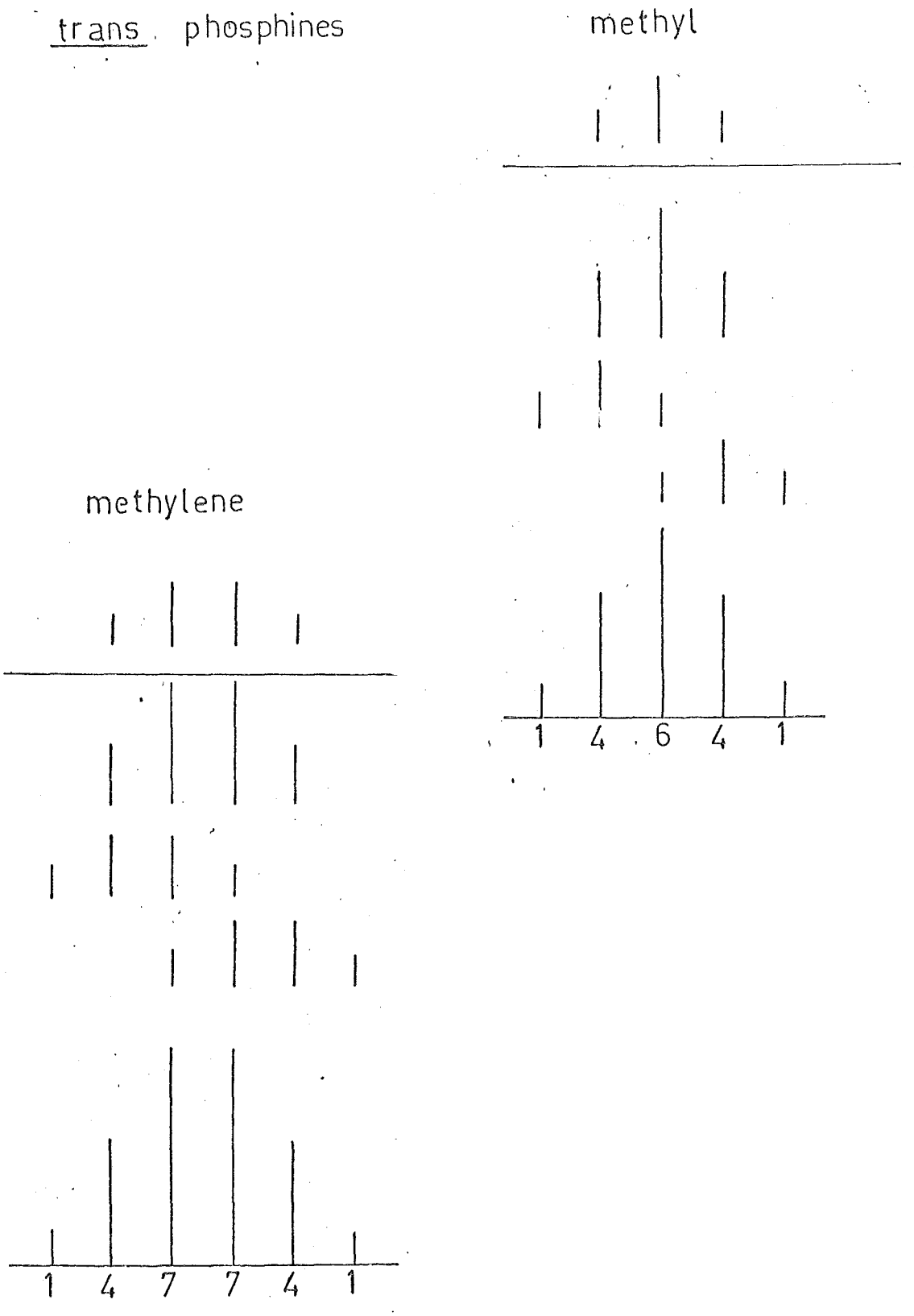
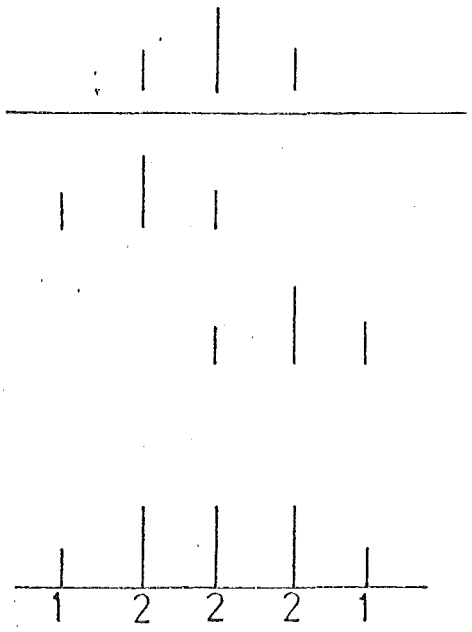


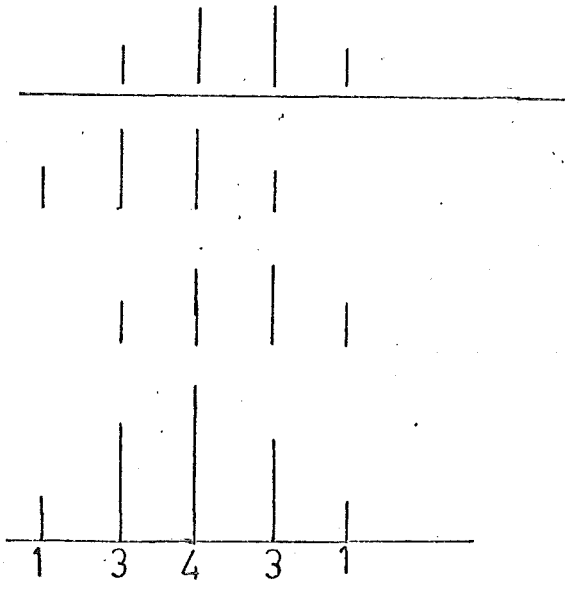
FIGURE 2·11 cont'd

<u>cis</u> phosphines

methyl



methylene



It is of interest that, in the platinum complexes, the methyl multiplet for the cis complexes shows no evidence of coupling with ^{195}Pt (spin $\frac{1}{2}$, natural abundance 33.8%); presumably the separation by four bonds is too great to allow such interaction to occur.

The methylene multiplet in the cis complexes can be considered to arise from the overlap of two 1:2:2:1 quartets as shown in Fig. 2.11, giving rise to a quintet of intensity ratio 1:3:4:3:1. The ^{1}H NMR spectrum of cis-$PtCl_2(Et_2PhP)_2$ (Fig. 2.9) shows a methylene multiplet which agrees well with this ratio. The value of $^{1}J(^{31}P-^{1}H)$ is approximately 7Hz . The multiplet lines show some evidence for a further slight coupling, probably due to ^{195}Pt, the extent of which is too small to be measured with any degree of certainty.

For trans complexes a more complicated situation is observed because of the effect on the spectra of the phenomenon of virtual coupling.[113] This arises when two phosphorus nuclei are in a trans environment in a complex. The two ^{31}P nuclei, each having a spin $\frac{1}{2}$, couple together very strongly in this situation; they are said to be "virtually coupled". For cis phosphorus nuclei virtual coupling is not observed and this has considerable importance for the assignment of stereochemistry.[63,114] Thus in the cis case, as discussed above, the multiplets arising from proton-proton coupling are split into two by interaction with ^{31}P. However for trans complexes the virtually coupled phosphorus nuclei split the proton multiplets into four sets of resonances and the combination of these gives rise to the observed intensity ratios. Thus for the methyl resonance the overlap of a 1:2:1 triplet of 1:2:1 triplets in the manner shown in Fig. 2.11 will result[112] in a quintet of intensity ratio 1:4:6:4:1. This ratio

is fulfilled to a good approximation in the spectra obtained for the trans complexes (see the spectra of the palladium complexes, Fig. 2.10). The value of $^{2}J(^{31}P-^{1}H)$ is approximately 17Hz .

In the case of the methylene multiplet the overlap of four 1:2:2:1 quartets can be expected to occur. As shown in Fig. 2.11 this can lead to a sextet of intensity ratio 1:4:7:7:4:1. Many of the spectra show this sextet pattern with the ratios rather variable although most are a good approximation to that expected. $^{1}J(^{31}P-^{1}H)$ is 7Hz approximately.

In the trans platinum complexes there is again some evidence in the methyl multiplet for a further small coupling interaction. This may be caused by coupling with ^{195}Pt, as noted above for the cis analogues.

The complexes trans-$PtCl_2(Et_2PhP)_2$ and trans-$PtBr_2(Et_2PhP)_2$ could not be obtained in a satisfactory crystalline form although there was evidence for their existence in solution. However, satisfactory spectra could not be obtained.

The triethylphosphite complexes studied have a cis configuration. As for the free ligand, the methyl resonance in the phosphite complexes is a 1:2:1 triplet showing no sign of coupling with ^{31}P. The methylene multiplet is a clearly defined quintet with intensity ratio 1:3:4:3:1, arising from the overlap of two 1:2:2:1 quartets with $^{1}J(^{31}P-^{1}H)$ approximately 7Hz . Both methyl and methylene multiplets are considerably deshielded as compared with those of the tertiary phosphine ligands. This is presumably a consequence of the presence of the electronegative oxygen atom which would have a marked electron withdrawing effect.

(b) Nickel (II) complexes:-

The ^{1}H NMR spectra of nickel (II) complexes consist of rather broad unstructured resonances at ambient temperature.

On the addition of a trace of free phosphine ligand the full multiplicity of the resonances is resolved and the same result is obtained when the spectra are run at lower temperature. A possible explanation for this effect may be that ligand dissociation is occurring in solution. This could cause the collapsing of multiplet structure at room temperature, while lower temperature would slow down the rate of dissociation, thus allowing the observation of the fine structure. The palladium (II) and platinum (II) complexes on the other hand (see later) have narrow line resonances and well-defined multiplets at all temperatures and in the presence of excess of ligand. Metal-phosphorus π -bonding may be more important for the latter complexes than for nickel (II), and hence ligand dissociation may be expected to be less likely.

For the diethylphenylphosphine complexes there is a large deshielding of the methylene multiplet and, to a lesser extent, the methyl multiplet. This can be ascribed to a structural isomerization in solution in which tetrahedral nickel (II) is formed. This species has two unpaired electrons and hence the large shifts can be explained by invoking paramagnetic contact interactions. The square planar-tetrahedral equilibrium for nickel (II) with mixed alkyl/aryl ligands has been the subject of extensive ^{1}H NMR[52-54] and electronic spectral[115] studies. As noted above, the nickel complexes studied in the present work are rather unstable with respect to ligand dissociation in chloroform solution and this instability increases with change of halogen from chlorine to iodine so that the spectrum of $NiI_2(PEt_3)_2$ could not be obtained. The chloro and bromo triethylphosphine complexes do not show any evidence for the paramagnetic contact shifts observed for the diethylphenylphosphine complexes. This is in line with the observation[48] that trialkylphosphine complexes of

TABLE 2.14

^{1}H NMR SPECTRA : Mononuclear trans-square planar complexes[(a)]

Compound	Methylene	Methyl	Phenyl	Ortho
PEt_3	-1.35	-1.07		
Et_2PhP	-1.60	-0.90	-7.26	-7.50
$NiCl_2(PEt_3)_2$	-1.67	-1.40		
$NiBr_2(PEt_3)_2$	-1.79	-1.36		
$NiCl_2(Et_2PhP)_2$	-3.58	-1.37	-7.55	
$NiBr_2(Et_2PhP)_2$	-6.36, -6.86	-1.60	-7.87	
$NiI_2(Et_2PhP)_2$	-6.10, -6.66	-1.80	-8.03	
$PdCl_2(PEt_3)_2$	-1.80	-1.12		
$PdBr_2(PEt_3)_2$	-1.97	.1.11		
$PdI_2(PEt_3)_2$	-2.18	-1.04		
$PdCl_2(Et_2PhP)_2$	-2.14	-1.10	-7.35	-7.67
$PdBr_2(Et_2PhP)_2$	-2.39	-1.10	-7.37	-7.67
$PdI_2(Et_2PhP)_2$	-2.60	-1.03	-7.40	-7.70
$PtCl_2(PEt_3)_2$	-1.93	-1.20		
$PtBr_2(PEt_3)_2$	-2.00	-1.17		
$PtI_2(PEt_3)_2$	-2.31	-1.10		
$PtI_2(Et_2PhP)_2$	-2.60	-1.08	-7.45	-7.60

(a) chemical shifts in ppm downfield from TMS

The centre of the resonance multiplet is the measured quantity

FIGURE 2·7

^{1}H NMR SPECTRA OF PEt_3 COMPLEXES

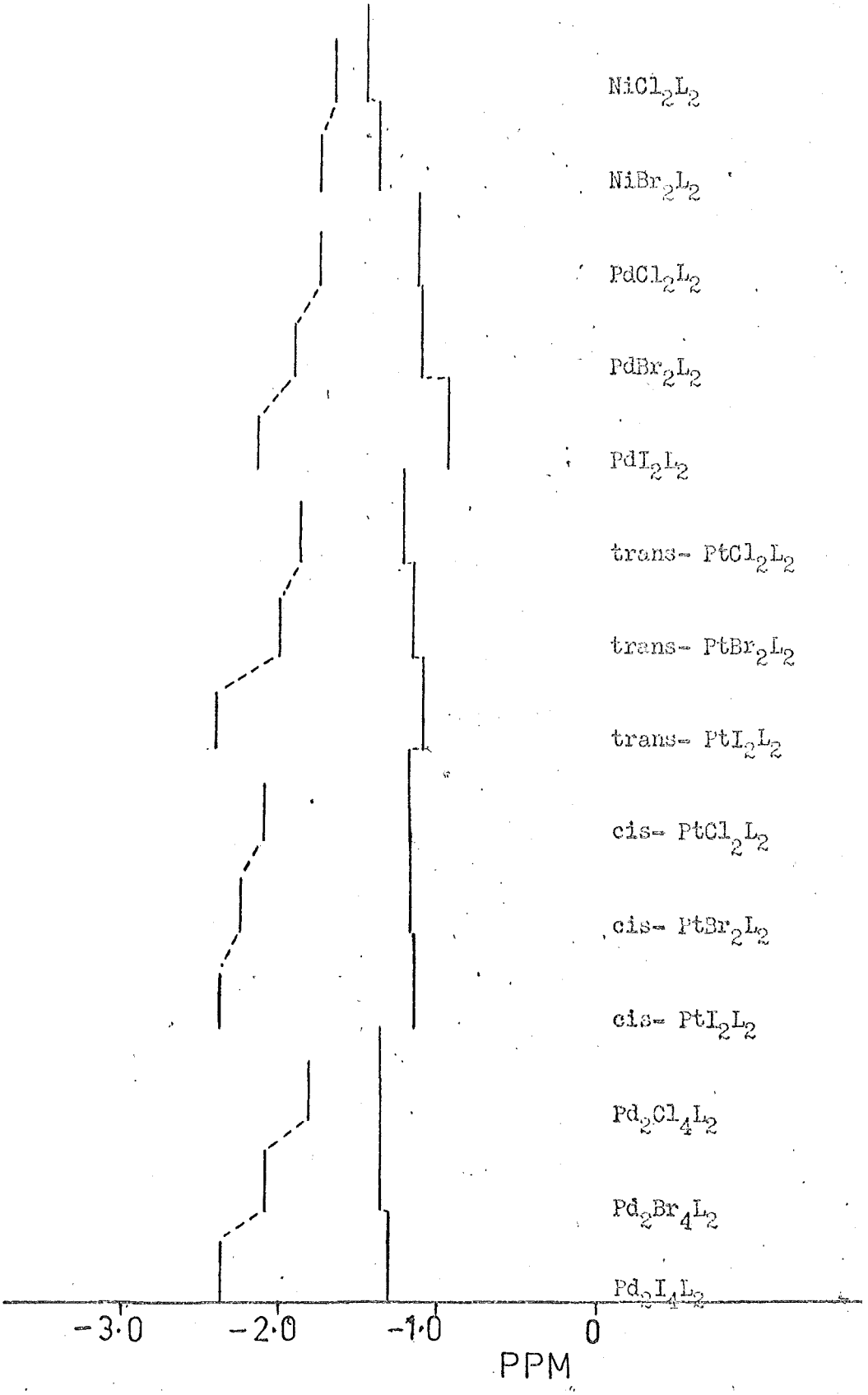


FIGURE 2·7 cont'd

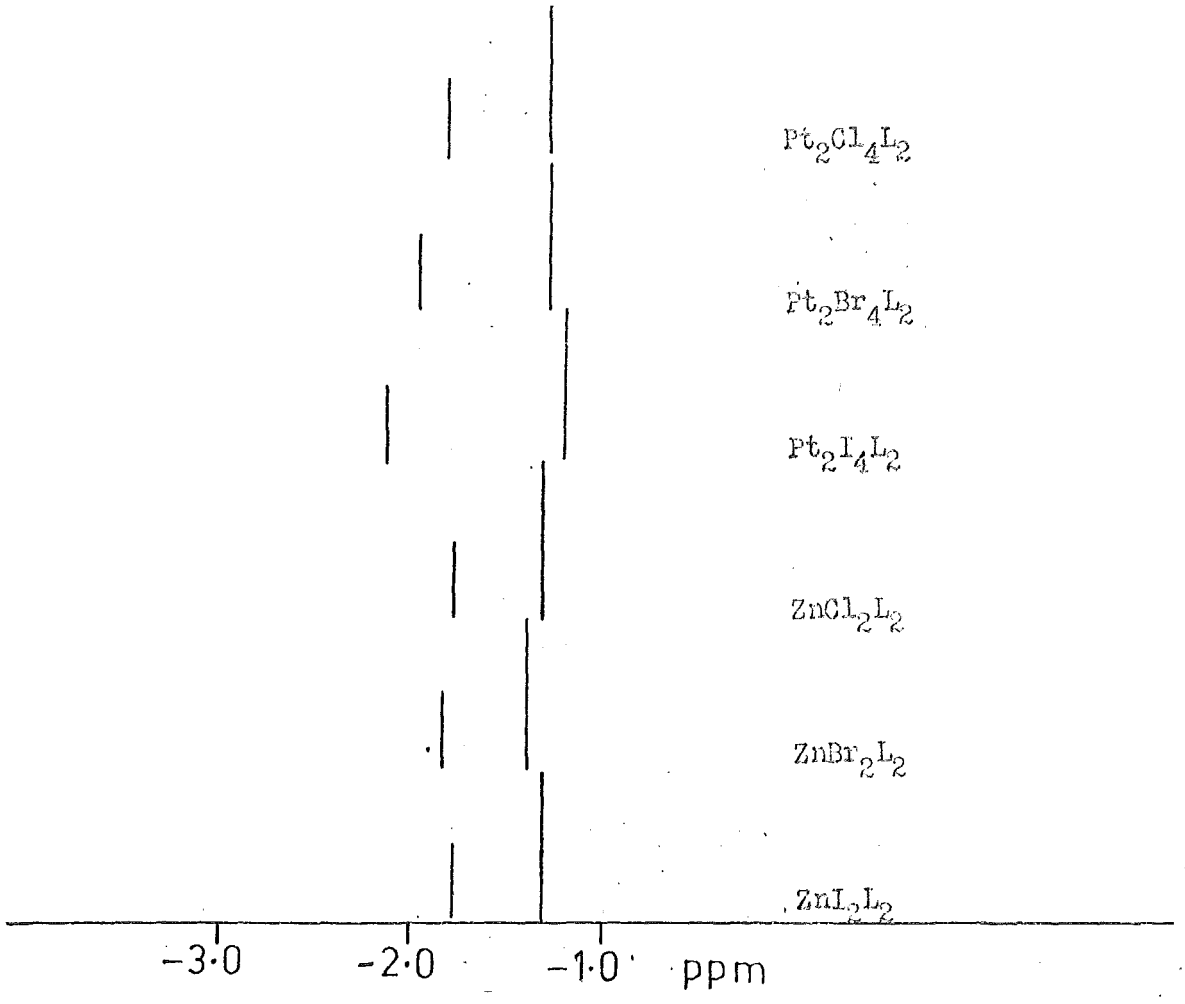
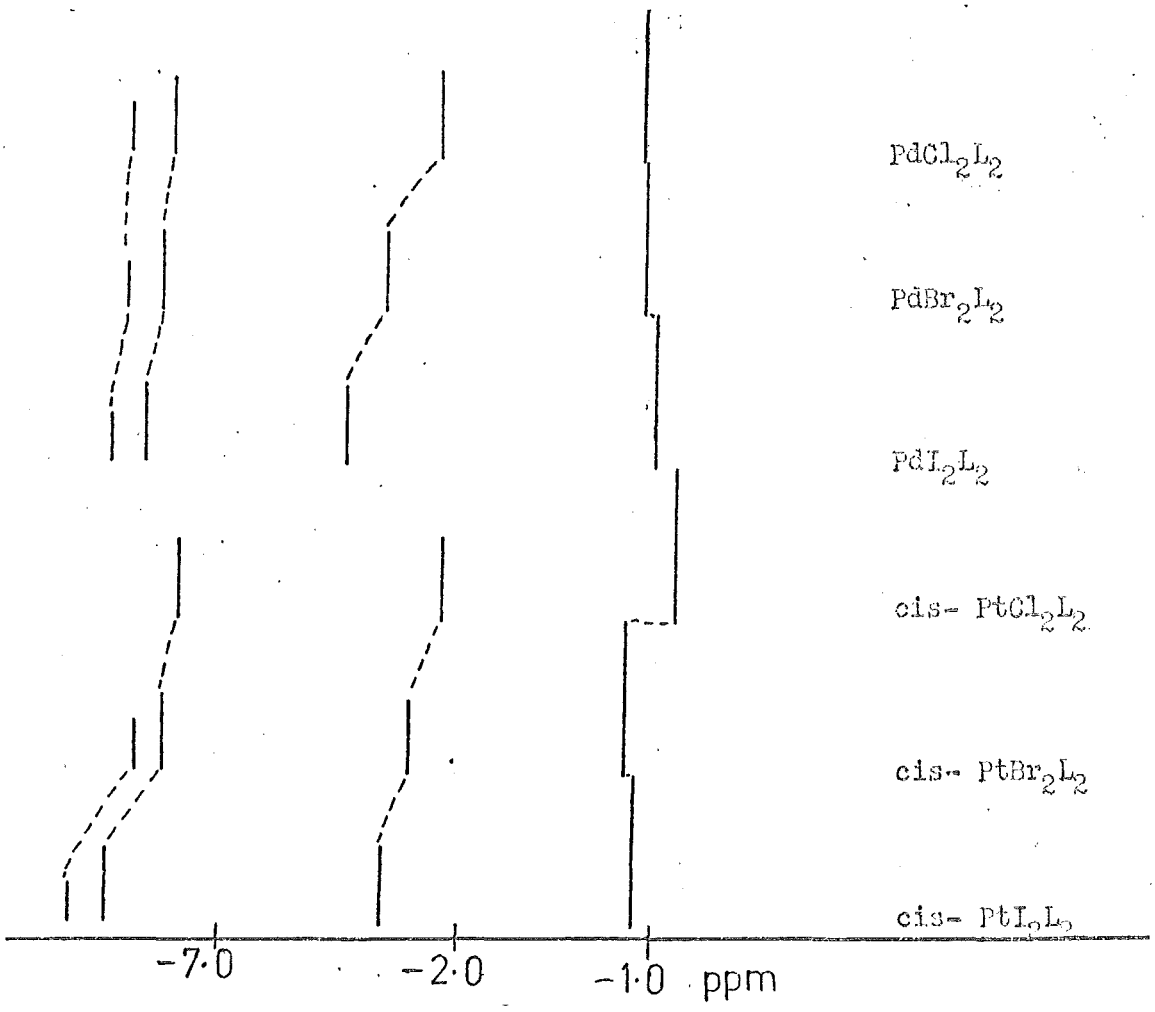


FIGURE 2·8

^{1}H NMR SPECTRA OF Et_2PhP COMPLEXES



nickel (II) are square planar both in the solid state and in solution. The chemical shifts of methyl and methylene resonances for $NiCl_2(PEt_3)_2$ and $NiBr_2(PEt_3)_2$ are given in Table 2.14 and Fig. 2.7. The methylene multiplet for the bromo complex is deshielded to a greater degree than the analogous chloro multiplet; the significance of this is considered below in relation to a similar observation for palladium and platinum complexes.

(c) Palladium (II) and platinum (II) mononuclear complexes:-

The ^1H NMR spectra of palladium (II) and platinum (II) in mononuclear square planar complexes give rise to spectral multiplets whose multiplicity can be interpreted in terms of the stereochemistry of the complexes (see earlier discussion, p. 40).

(i) Methyl and methylene multiplets:- Coordination effects

A difference is expected between the chemical shifts of protons in the free and coordinated ligands since coordination will result in the donation of the phosphorus lone pair of electrons into a vacant metal orbital thus making the phosphorus atom more electropositive. Drift of electron density from the organic groups may therefore be expected, in order to compensate for the increased positive charge on the phosphorus, and this leads to the observed deshielding (see Tables).

It is of interest that the initial chemical shift change on coordination for both methyl and methylene protons is greater for cis complexes as compared with the trans analogues. This may be related to the greater metal-phosphorus bond strength in the cis case,[30,31] as already discussed in relation to the far infra-red spectra of square planar complexes (p. 28). The drift of electrons from the organic groups on phosphorus, and hence the deshielding of the protons, will be greater for the

TABLE 2.15

^{1}H NMR Spectra : mononuclear cis square planar complexes[a]

Compound	Methyl	Methylene	Phenyl	Ortho
$PtCl_2(PEt_3)_2$	-1.17	-2.10		
$PtBr_2(PEt_3)_2$	-1.16	-2.17		
$PtI_2(PEt_3)_2$	-1.16	-2.30		
$PtCl_2(Et_2PhP)_2$	-0.90	-2.03	-7.33	-7.33
$PtBr_2(Et_2PhP)_2$	-1.13	-2.16	-7.40	-7.50
$PtI_2(Et_2PhP)_2$	-1.11	-2.16	-7.65	-7.83

(a) chemical shifts in ppm downfield from TMS the centre of the resonance multiplet is the measured quantity

TABLE 2.16

^{1}H NMR Spectra : binuclear complexes [a]

Compound	Methyl	Methylene
$Pd_2Cl_4(PEt_3)_2$	-1.28	-1.85
$Pd_2Br_4(PEt_3)_2$	-1.28	-2.10
$Pd_2I_4(PEt_3)_2$	-1.25	-2.30
$Pt_2Cl_4(PEt_3)_2$	-1.20	-1.83
$Pt_2Br_4(PEt_3)_2$	-1.20	-1.93
$Pt_2I_4(PEt_3)_2$	-1.17	-2.10

(a) chemical shifts in ppm downfield from TMS the centre of the resonance multiplet is the measured quantity

stronger metal-phosphorus bond since the phosphorus will presumably be more electropositive in this case.

The effect of change in halogen. The most obvious comparison that can be made between a typical set of three analogous complexes differing only in halogen is the increased deshielding of the methylene multiplet from chloro to bromo to iodo complexes. The methyl multiplet by comparison stays either relatively constant (cis complexes) or experiences a small but consistent upfield shift (trans complexes) for the same order of halogen change as above.

In the case of the shift of the methylene resonances with change in halogen in the order Cl, Br, I several explanations appear possible. The first concerns the increasing size of the halogens in the above order. The magnetic influence of an intramolecular interaction between lone pairs on the halogens and the organic groups on the tertiary phosphine ligands might produce the observed chemical shift changes. This explanation is not however supported by the results found for the zinc (II) complexes which will be discussed shortly. Also, as previously discussed for the far infra-red spectra of these complexes, the non-bonded interactions between halogeno- and phosphine ligands appear to be greater in cis complexes as compared with trans analogues, as shown by molecular models. Thus if the deshielding phenomenon is caused by intramolecular non-bonded interactions it should presumably be greater in the cis complexes. However, as shown in Tables 2.14 and 2.15, the degree of deshielding with change of halogen is greater for the trans complexes than for the cis analogues, and hence it seems unlikely on this basis that non-bonded interactions can be the cause of the observed deshielding changes.

A further possible explanation for the trends in the methylene multiplet involves a modification of electron density in the complexes through a metal to halogen $M_{d\pi} \longrightarrow X_{d\pi}$ bonding mechanism. The π acceptor ability for the halogeno-ligands is considered to increase in the order chlorine < bromine < iodine (see Chapter 1, p. 4). The effect of a metal to halogen $M_{d\pi} \longrightarrow X_{d\pi}$ interaction would be to increase the positive charge on the metal ion, thus increasing the attraction of the metal ion for charge from the other ligands. Thus there is a likelihood of charge draw-off from the phosphine ligands by this mechanism and this will increase in the order of π acceptor ability of the halogens. Consequently this explanation predicts an increasing deshielding of the methylene protons with change in halogen in the order Cl, Br, I , as is observed in the present work. This explanation has been advanced before to explain similar effects in the ^{1}H NMR spectra of sulphide complexes[25,26], and in carbonyl complexes of ruthenium and iridium with tertiary phosphine ligands.[116-118] The postulated increase in $M_{d\pi} \longrightarrow X_{d\pi}$ bonding in the order Cl, Br, I will also have the important effect of reducing the extent of metal to phosphorus $d\pi - d\pi$ back donation, and this effect would help to enhance the observed deshielding since less charge is available to be delocalized onto phosphorus by the back donation mechanism.

The trends in polarizability of the halogens may also be used to account for the deshielding changes discussed above, rather than invoking π -bonding. This polarizability is considered to increase in the order chlorine < bromine < iodine (Chapter 1, p. 4). The result of polarization will be an increase in negative charge on the side of the halogen atom adjacent to the metal. As a consequence the metal ion will

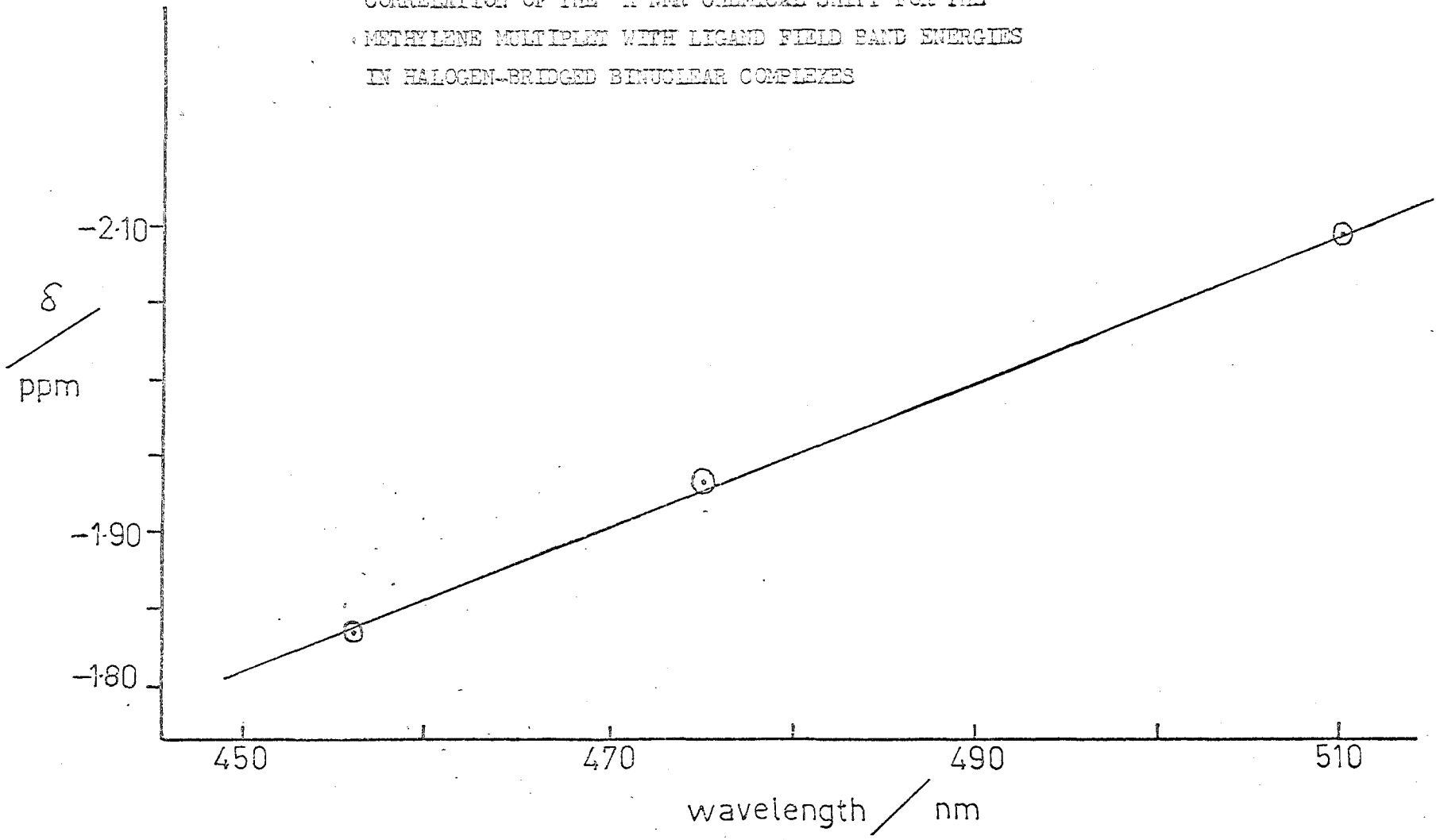
become more electropositive, this effect increasing with increased halogen polarizability. Therefore the electron drift from the phosphine ligands may be considered to increase in the same order, with consequent increased deshielding of the protons on the organic groups of the phosphines. This explanation is not however supported by results found for zinc (II) complexes (p. 52) where there is virtually no change in methylene proton chemical shift with halogen change in the order Cl, Br, I.

An important criticism of the above explanations in terms of either metal to halogen $M_{d\pi} \longrightarrow X_{d\pi}$ bonding or halogen polarizability trends is that the magnetic anisotropies of the metal-ligand bonds have not been considered. The magnetic effect of circulating electrons can contribute considerably to proton chemical shifts.[119] However the phenomenon is not well characterised for metal-ligand bonds, although Goggin et al.[72] have calculated that the effect should increase in the order $Cl < Br < I$ which is the same order as the deshielding trend in the methylene multiplet.

While the magnetic anisotropies of the metal-ligand bonds may have a significant effect in these complexes, the transition metal ions may themselves exhibit a paramagnetic anisotropy. Van Vleck[120] proposed that transition metal ions possessing incompletely filled d levels with all electrons spin paired in the ground state, may exhibit a weak paramagnetism in a magnetic field, which derives from mixing of the ground state energy level with low lying excited states. Ramsay[121] extended these ideas to a discussion of the possible paramagnetic contributions to NMR shielding parameters as a result of the mixing of states. In the present work the d^8 metal ions could be susceptible to this effect and further, the effect should be related to the order of

FIGURE 2·14

CORRELATION OF THE ^{1}H NMR CHEMICAL SHIFT FOR THE METHYLENE MULTIPLET WITH LIGAND FIELD BAND ENERGIES IN HALOGEN-BRIDGED BINUCLEAR COMPLEXES



ligand field stabilisation for the halogeno- ligands. Thus one would expect the paramagnetic contribution to the deshielding of ^{1}H NMR resonances to increase in the order Cl,Br,I, as is observed. It has been pointed out by Miller et al.[122] that the deshielding changes ought to correlate with the energies of the ligand field bands in the visible spectra and these workers have demonstrated such a correlation for complexes of the form trans-X(2-vinylphenyl)bis(triethylphosphine) nickel (II). The extension of this correlation to palladium (II) and platinum (II) complexes was ruled out since the ligand field transitions in these cases are masked by intense charge transfer bands at relatively low energy.[122] In the present work only nickel (II) and binuclear platinum (II) complexes gave electronic spectra where the ligand field bands were not obscured. In addition, the complex $NiI_2(PEt_3)_2$ was unstable with respect to ligand dissociation in solution and hence a ^{1}H NMR spectrum of this complex could not be obtained. Thus a correlation of NMR chemical shifts with ligand field band energies was only possible for the $Pt_2X_4(PEt_3)_2$ complexes. Fig. 2.14 shows that there is a linear correlation. For the ruthenium (II) complexes (Chapter 4) it was again not possible to observe the ligand field bands in the electronic spectra because of interference of intense low energy charge transfer bands. Thus the interesting premise of Miller et al.[122] cannot be fully investigated in the present work.

The deshielding of the methylene multiplet can thus be considered from a variety of approaches. However, the explanation given earlier in terms of the influence of $M_{d\pi} \longrightarrow X_{d\pi}$ bonding receives support from other observations. As the tables of chemical shifts and the diagrammatic representations show, change in metal from nickel to palladium to platinum produces an increase

in the deshielding of the methylene multiplet with the same halogen, and for complexes with the same stereochemistry. This is in line with an improved π-bonding ability for the transition metals down a group.

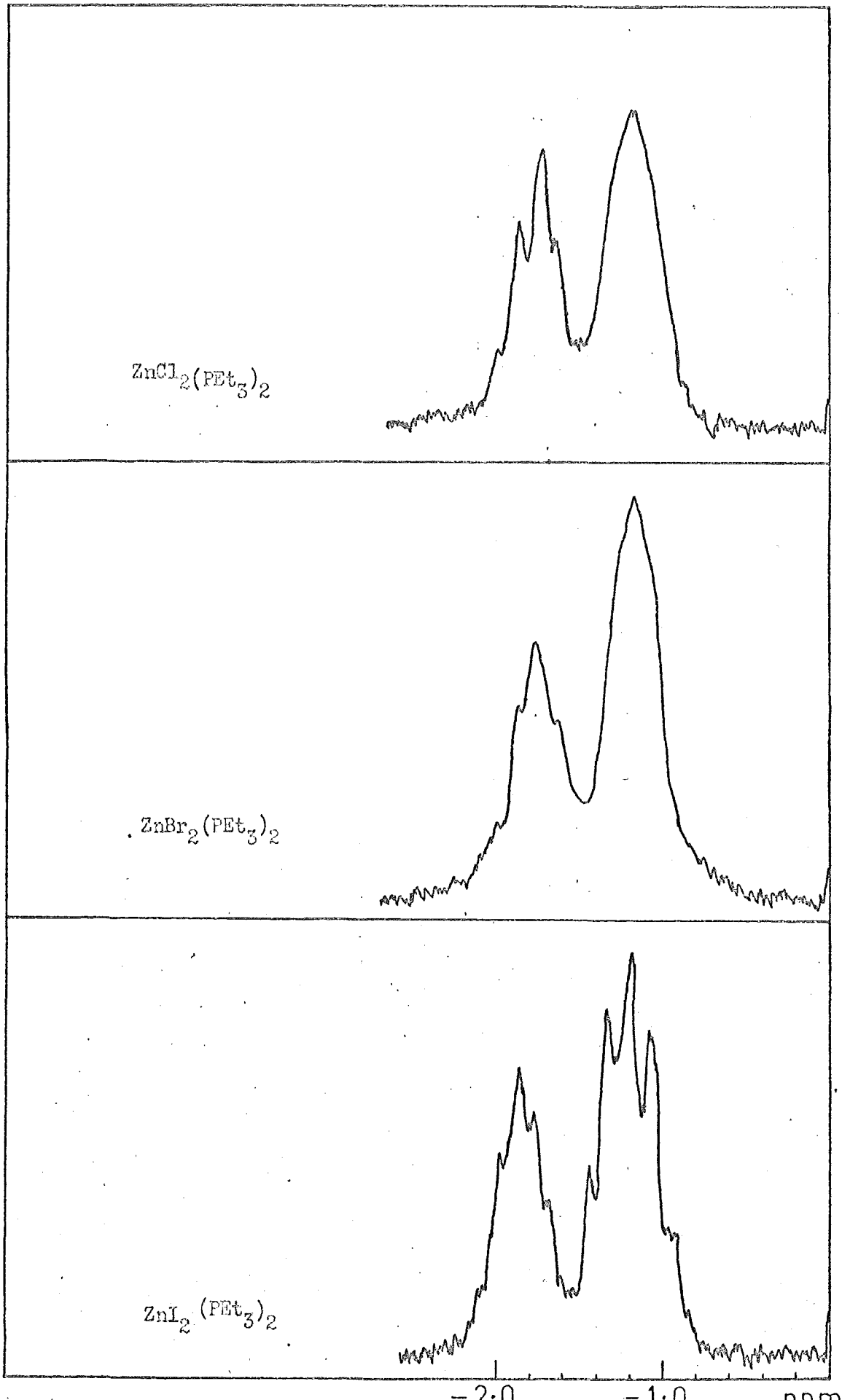
For cis - platinum complexes, as compared with the trans analogues, the increase in deshielding of the methylene multiplet with halogen change is somewhat smaller (Table 2.15 and Fig. 2.17). This may be explained in terms of a competition for metal d orbitals between phosphine and halogeno-ligands (mutually trans) in the cis complexes, with the smaller deshielding indicating that phosphorus is a better π-acceptor.

It has been mentioned earlier (p. 44) that the trend in the methyl multiplet chemical shift with halogen change is generally a small shift to higher field. This might be explained on the basis of a greater non-bonded interaction of the halogeno-ligands with the methyl protons, with this interaction being smaller for the methylene protons. If this is so then the intramolecular interactions in the methyl case can be considered to be greater than the intermolecular electronic effects, thus leading to the observation of a trend in chemical shifts in the reverse order as compared with the methylene protons.

(ii) Phenyl resonances:- The phenyl proton resonance multiplets in diethylphenylphosphine complexes also shift with change in halogen. For palladium the multiplet is increasingly deshielded (Table 2.14, 2.15), to a small extent (0.05 ppm from Cl to I), with change in halogen in the order Cl,Br,I. For platinum complexes the shift is greater (0.32 ppm from Cl to I). The multiplets are themselves split into two groups of resonances in most cases, with an integrated intensity ratio of approximately 2:3. The smaller area multiplet lying furtherest downfield may

FIGURE 2·12

^{1}H NMR SPECTRA OF ZINC COMPLEXES



be tentatively assigned to the resonance of the ortho protons. While this multiplet is invariant for the palladium complexes it displays an increased deshielding with change in halogen for the platinum case. Similar explanations to those used above for the variation in the methylene multiplet with different halogens may be applied here.

(iii) Triethylphosphite complexes:- It is of interest that for the triethylphosphite complexes of platinum (II) a similar deshielding effect with change in halogen is observed as for the analogous cis - platinum (II) tertiary phosphine complexes (see Tables 2.15, 2.17). Apparently the interposing of the oxygen atom has little effect on the deshielding phenomenon, and the magnitude of the effects in phosphite and phosphine complexes is very similar.

(iv) Complexes of the ligand (p-methoxyphenyl) diethylphosphine:- In order to study further the influence of the metal and halogen on the ^{1}H NMR spectra of tertiary phosphine ligands, palladium (II) complexes of the ligand (p-methoxyphenyl) diethylphosphine have been prepared in the present work. The spectrum of the free ligand is reproduced in Fig.6.1(p. 179) in connection with studies of the complexes of para-substituted phenyldiethylphosphines with ruthenium (II). Table 2.17 contains ^{1}H NMR data for the free ligand and for the palladium (II) complexes.

In the free ligand the phenyl region is quite markedly affected by the mesomeric electron donation from the +R para-methoxy substituent. As shown in Fig. 2.13 the release of electrons from the methoxy group will result in an increase in charge at the position meta to the phosphorus atom, and a decrease in charge at the position ortho to the phosphorus.

TABLE 2.17

^{1}H NMR SPECTRA : $P(OEt)_3$ and $(p\text{-MeOPh})Et_2P$ complexes [a]

Compound	methylene	methyl	methoxy	phenyl meta	phenyl ortho
$(p\text{-MeOPh})Et_2P$ (=L)	-1.50	-0.97	-3.47	-6.70	-7.20
$PdCl_2L_2$	-2.10	-1.13	-3.87	-7.00	-7.70
$PdBr_2L_2$	-2.28	-1.08	-3.87	-6.97	-7.63
PdI_2L_2	-2.52	-1.03	-3.82	-6.90	-7.50
$P(OEt)_3$	-3.80	-1.20			
cis-$PtCl_2(P(OEt)_3)_2$	-4.06	-1.27			
cis-$PtBr_2(P(OEt)_3)_2$	-4.28	-1.37			
cis-$PtI_2(P(OEt)_3)_2$	-4.23	-1.33			

(a) chemical shifts in ppm downfield from TMS
the centre of the resonance multiplet is the measured quantity

TABLE 2.18

^{1}H NMR SPECTRA : Zinc (II) complexes [a]

Compound	Methylene	methyl	phenyl
$ZnCl_2(PEt_3)_2$	-1.80	-1.22	
$ZnBr_2(PEt_3)_2$	-1.83	-1.27	
$ZnI_2(PEt_3)_2$	-1.83	-1.22	
$ZnBr_2(Et_2PhP)_2$	-2.05	-1.08	-7.43
$ZnI_2(Et_2PhP)_2$	-2.07	-1.08	-7.40

(a) chemical shifts in ppm downfield from TMS
the centre of the resonance multiplet is the measured quantity

These electronic effects are reflected in the spectra by the appearance of two regions of phenyl proton resonance, the higher field doublet ($^1J(^1H-^1H)$ = 9Hz) corresponding to the protons meta to P and the lower field multiplet to the protons ortho to P. The methoxy protons resonate as a single sharp peak near - 3.5 ppm. The ethyl region shows quintets for both methyl and methylene protons, arising from coupling with ^{31}P. Relevant coupling constants are $^2J(^{31}P-^1H)$ = 16Hz (methyl) and $^1J(^{31}P-^1H)$ = 14Hz (methylene).

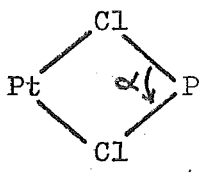
The essential features of the free ligand spectrum are preserved upon coordination although all resonances undergo significant shifts to lower field. Compared with the effect of coordination on the unsubstituted Et_2PhP ligand (Table 2.14) the effects here on the phenyl proton resonances are larger. Thus the meta protons shift c a. - 0.3 ppm, the ortho protons by c a. -0.5 ppm, and the methoxy protons by c a. -0.4 ppm. This may reflect the greater charge available to the metal ion when the phenyl ring contains a mesomeric electron - donating substituent.

With change in halogen the methyl and methylene resonances show similar trends to the palladium complexes with Et_2PhP as ligand, as might be expected. The methoxy resonance is essentially constant with halogen change. Both phenyl proton multiplets show a small but consistent deshielding on change in halogen in the order Cl,Br,I. This trend is the opposite of that found for the phenyl protons of complexes of Et_2PhP.

(d) Binuclear square planar complexes:-

The six complexes, $M_2X_4(PEt_3)_2$ where M is Pd or Pt, also show the increased deshielding of the methylene multiplet of the phosphine ligand with halogen change in the order Cl,Br,I, as

discussed above for mononuclear complexes (see Table 2.16), and no doubt similar explanations are equally valid here. It is of interest that for these binuclear complexes the initial deshielding of the methyl multiplet upon coordination is now considerably larger than is the case for mononuclear complexes (see Tables 2.14 - 2.16). A similar situation is observed for the analogous multiplet in zinc complexes (see later). The explanation of this effect may lie in the reduced non-bonded interactions which occur between tertiary phosphine and halogeno-ligands in these complexes. The single crystal X-ray structure[83] of the complex $Pt_2Cl_4(PPr_3)_2$ shows that the coordination about each platinum atom is no longer strictly square. Apparently the dihalogeno bridge imposes stereochemical restraints on the molecule and there is more space available to the phosphine ligands. This is manifested in an angle, α, of 83.6° between the bridging chlorines and platinum

i.e. 

The greater space available to the organic groups on phosphorus presumably results in less intramolecular interaction with the halogens, and hence allows the intermolecular electronic effects to become dominant, leading to a larger deshielding.

The phosphine ligands in these binuclear complexes, while, at least formally, <u>trans</u> to each other, have the dihalogen bridge intervening and virtual coupling between the ^{31}P nuclei does not occur. Thus the spectra show coupling with a single phosphorus nucleus. Coupling constants are similar to those found for <u>cis</u> mononuclear systems i.e. approximately 19Hz for $^2J(^{31}P\text{-}^1H)$ in the methyl multiplet and 7Hz for $^1J(^{31}P\text{-}^1H)$ in the methylene case.

<u>The spectra of tetrahedral zinc (II) complexes</u>:-

Like the nickel (II) case discussed previously the

^{1}H NMR spectra of zinc (II) complexes give broad resonances showing little structure at room temperature. At lower temperatures or on addition of excess ligand, however, the full multiplicity becomes apparent. As discussed for the nickel (II) complexes (p. 42) ligand dissociation may result in the collapse of multiplet structure into a single broad peak for each proton environment. Zinc-phosphorus π -bonding is not expected to be important, firstly since the filled 3d orbitals of zinc are tightly bound to the nucleus and are not readily available for $d\pi$ -$d\pi$ bonding, and secondly since the tetrahedral structure of these complexes implies that the spatial orientation of the filled 3d orbitals is not so suitable for π -bonding in any case. As the size of the halogeno-ligand increases, the spectral multiplets show more structure and at room temperature the complex $ZnI_2(PEt_3)_2$ shows a well-defined quintet methyl resonance. This can be related to the greater stability with respect to ligand dissociation of these complexes[90] as the halogeno-ligand changes in the order Cl,Br,I.

The effect of coordination on the methyl proton resonance of the tertiary phosphines is similar to that discussed previously for the binuclear complexes. Thus a large deshielding is observed and this can be related to the lessened intramolecular interactions of phosphine and halogeno-ligands in these tetrahedral complexes as discussed previously (p. 51).

The most notable feature of the spectra of the zinc complexes is the invariance in position of both methyl and methylene multiplets with change in halogen. As Table 2.18 and Figs. 2.7 and 2.12 show there is only a slight shift downfield for the methylene resonance between bromo and iodo diethylphenylphosphine complexes ($ZnCl_2(Et_2PhP)_2$ could not be isolated), and a similar

slight shift in the methylene position between chloro and bromo PEt_3 analogues. There is no change at all between $ZnBr(PEt_3)_2$ and $ZnI_2(PEt_3)_2$.

The principal difference between a Group II b element such as zinc and the transition elements nickel, palladium and platinum is that the filled 3d orbitals of zinc are tightly bound to the nucleus and their use in forming π-bonds is considered unlikely. This has been discussed by Nyholm.[123] Also, the zinc complexes are tetrahedral in structure (whereas the d^8 transition metal complexes are square planar), and in such an environment π-bonding is likely to be less important. Hence, at first sight, the relative constancy of the chemical shift of the methylene and methyl multiplets with change in halogen lends support to the $M_{d\pi} \longrightarrow X_{d\pi}$ bonding hypothesis advanced to explain the trends in transition metal complexes, where the d orbitals are less tightly bound to the nucleus and are more readily available for π-bond formation.

However, the possible intramolecular magnetic interaction of the halogen lone pairs would be reduced for the tetrahedral zinc complexes. Hence, at least on the basis of this simple stereochemical argument, one cannot use the constancy of the zinc resonances in support of the absence of an intramolecular magnetic interaction in the square planar complexes, where the halogen-phosphine distance is less. There is, however, some evidence from structural studies that the comparison of formally tetrahedral and square planar stereochemistries may be valid. Thus many zinc complexes are considerably distorted from tetrahedral stereochemistry towards a pseudo-planar structure. It is unfortunate that in this respect little structural data are available for phosphine complexes of zinc (II). The structure of the anion $[ZnBr_3(Ph_3P)]^-$ has been

determined recently.[124] The coordination about zinc is distorted tetrahedral with the angles between the bromines of the order of 120°. Structures with various nitrogen donor ligands (mainly substituted pyridines) have been studied quite extensively. For example, in dichlorobis (4-methylpyridine) zinc (II)[125] the coordination about zinc is again distorted tetrahedral, with a large Cl- Zn-Cl angle of 121.8°. This was attributed to repulsions between non-bonded electrons on the chlorines. Similar large values have been reported for this angle in $Zn(py)_2Cl_2$, 121.0° [126]; and dichlorobis (1-methyltetrazole) zinc (II), 118.4°.[127] This large bond angle may be general and therefore it is probable that a similar significant distortion exists for the dihalogenobis(phosphine)zinc (II) complexes studied in the present work. It can be recalled from previous discussion (p. 29) that cis-$PtCl_2(PMe_3)_2$ has been shown[37] to be significantly distorted from true square planar geometry towards a tetrahedral structure, but there is still a significant deshielding of the methylene multiplet with change in halogen for the ^1H NMR spectra of cis-platinum complexes.

In summary then, it seems likely that the non-bonded interactions in cis square planar complexes will be comparable to those in pseudo-tetrahedral zinc (II) complexes and this would seem to make the explanation in terms of intramolecular magnetic interaction of the organic groups and the halogeno ligands less likely. The real caution must come from applying solid state arguments to solution phenomena, and in not considering the possible effects of metal-ligand bond anisotropy in these complexes. A more general discussion of these results when compared with those from other systems will be given in Chapter 5.

2.2.3 Carbon-13 Nuclear Magnetic Resonance Spectra

(a) Introduction:-

The ^{13}C NMR spectra of the complexes have been obtained in deuteriochloroform solution. The spectra were run with proton noise decoupling which decouples out the proton interaction with the ^{13}C nuclei. Further, since the natural abundance of the carbon-13 isotope is 1.11% there is a negligible chance of two ^{13}C nuclei being adjacent to each other in an organic group of one of the phosphines employed in this work. Therefore ^{13}C-^{13}C coupling is not observed in the ^{13}C NMR spectra of these complexes, which are not isotopically enriched. These features therefore combine to make the spectra relatively simple. Spectral assignments are given in Tables 2.19-2.21 and Figures 2.18-2.20. portray some representative spectra.

(b) Some theoretical observations:-

One early application of ^{13}C NMR spectroscopy in the study of phosphine complexes was in the elucidation of stereochemistry.[73] It was proposed that virtual coupling of phosphorus nuclei in trans phosphine complexes should give rise to a 1:2:1 triplet resonance pattern in the ^{13}C NMR spectrum, and that a 1:1 doublet should be observed for cis phosphine complexes. This is therefore analogous to the situation in ^{1}H NMR spectra where virtual coupling occurs for trans, but not for cis, phosphorus nuclei, with consequently different multiplet resonance patterns for the two cases (see p. 39). However, it has recently been pointed out[74,128,129] that the total spin systems for ^{1}H and ^{13}C nuclei in phosphine complexes in general will be of different types. Thus for protons the spin system is $A_nXX'A_n'$ (where A = ^{1}H and X = ^{31}P), while for carbon-13 the spin system is AXX' (A = ^{13}C, X = ^{31}P) due to the

low natural abundance of the carbon-13 isotope. On the basis of these differing spin systems it has been further shown[74] that smaller values of Jpp will satisfy the necessary conditions for the observation of a triplet resonance pattern in ^{13}C NMR spectra than for its observation in ^{1}H spectra. In trans phosphine complexes typical values of Jpp are of the order of 500Hz [74] and this value is certainly large enough to produce triplet resonances in both ^{1}H and ^{13}C NMR spectra. For cis phosphine complexes Jpp is in general much smaller, ranging typically from 0 to 50 Hz .[74] When Jpp is zero doublets will be observed for both ^{1}H and ^{13}C spectra; however, when Jpp is small but not zero (say approximately 20Hz) the ^{13}C spectrum will give rise to a multiplet intermediate between a 1:1 doublet and a 1:2:1 triplet, while the ^{1}H NMR spectrum will still show a 1:1 doublet. As noted above this can be related[74] to the different total spin systems for the respective nuclei. For larger values of Jpp (approx. 50Hz) cis - phosphine complexes will show a well-defined triplet (although not a 1:2:1 triplet) in their ^{13}C spectra, while still showing a 1:1 doublet in the proton case. It is therefore invalid to assume that the appearance of triplets in ^{13}C NMR spectra necessarily implies a trans-phosphine stereochemistry and this demonstrates the need for caution in interpretation of the ^{13}C NMR spectra of phosphine complexes. The more clear cut situation for ^{1}H NMR spectra therefore makes stereochemical assignment more reliable for proton spectra.

(c) ^{13}C spectra of the phosphine ligands:-

The ^{13}C spectra of a large number of tertiary phosphines (including PEt_3 and Et_2PhP) have been discussed by Mann.[130] The spectra obtained in the present work for PEt_3 and Et_2PhP are shown

TABLE 2.19

^{13}C NMR spectra of phosphine ligands[a]

Compound	methyl	methylene	C_1	C_{ortho}	C_{meta}	C_{para}
PEt_3	-9.7 d (14.0)	-19.1 d (13.8)				
Et_2PhP	-10.0 d (15.0)	-20.4 d (12.0)	.139.2 d (18.0)	-132.5 d (18.0)	-128.4 d (6.0)	-128.5 s

(a) chemical shifts in ppm downfield from TMS

coupling constants (Hz) in parentheses

s = singlet ; d = doublet

FIGURE 2·15

NOMENCLATURE FOR PHENYL RING CARBON ATOMS

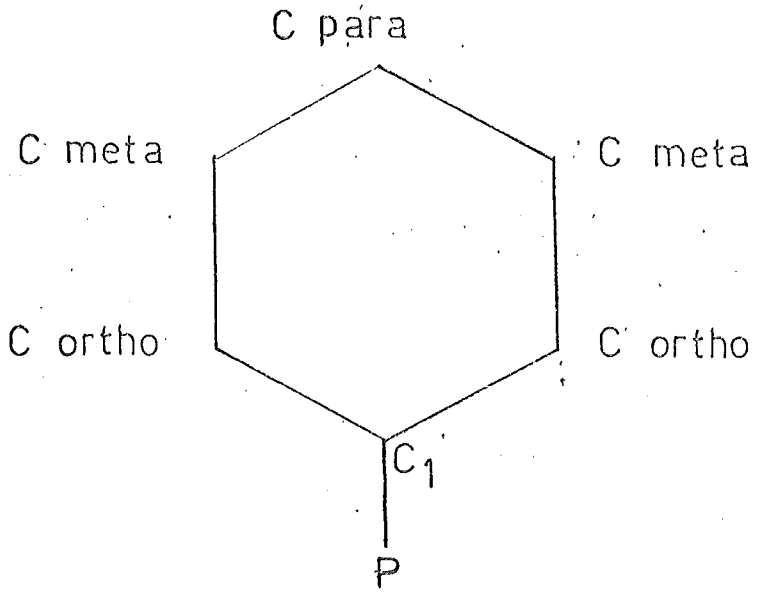


FIGURE 2·16

^{13}C NMR SPECTRA OF PEt_3 COMPLEXES

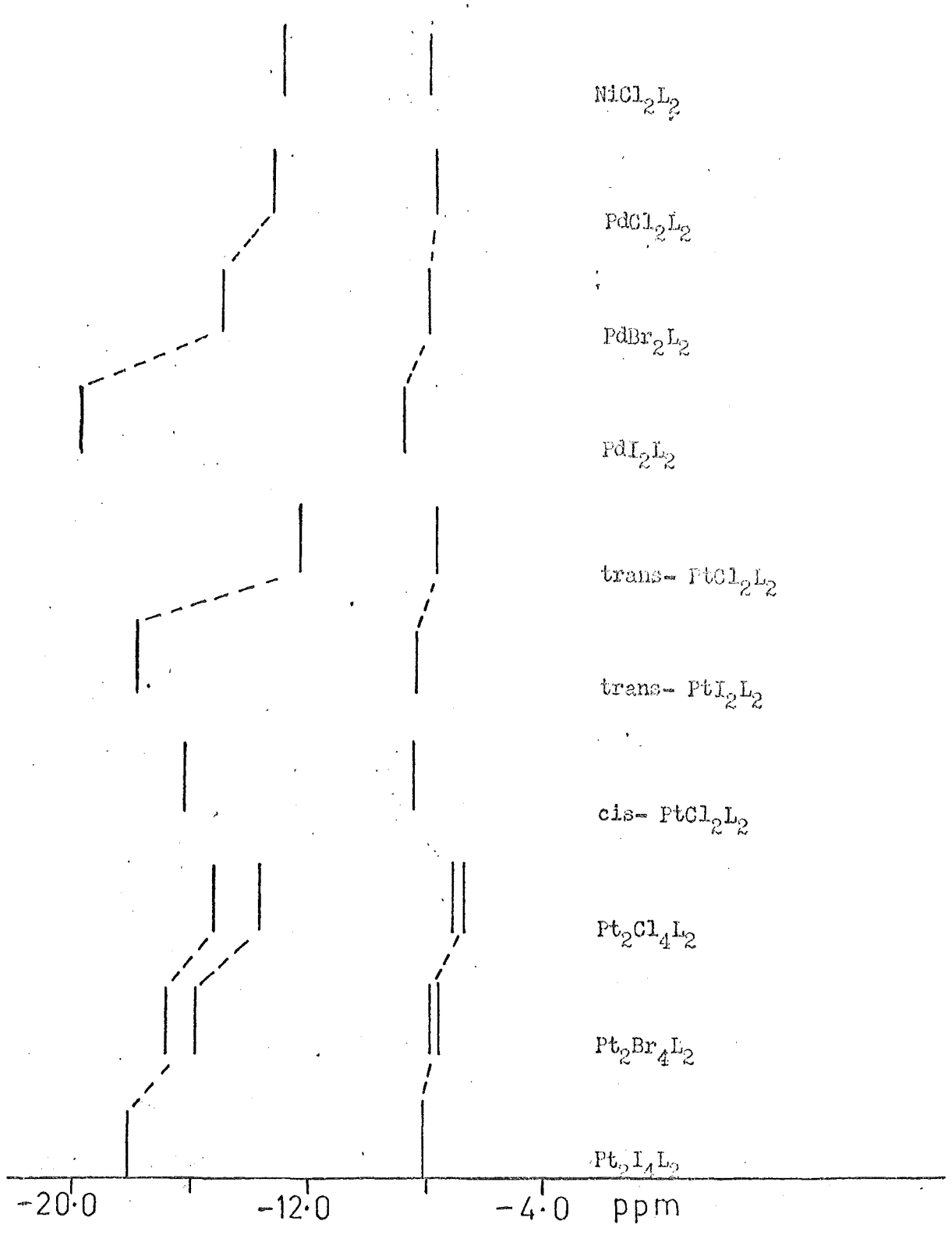


FIGURE 2·16 cont'd

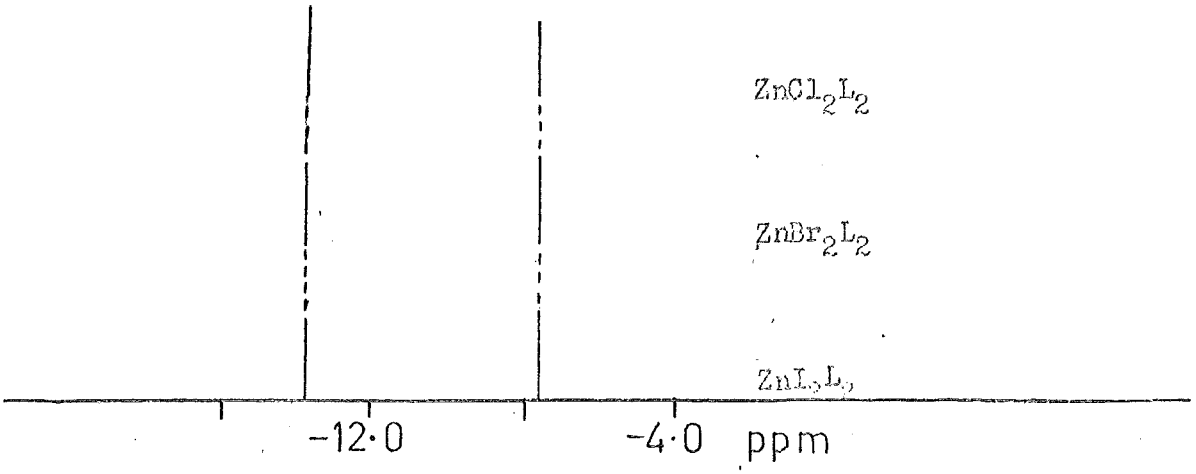


FIGURE 2·17

^{13}C NMR SPECTRA OF Et_2PhP COMPLEXES

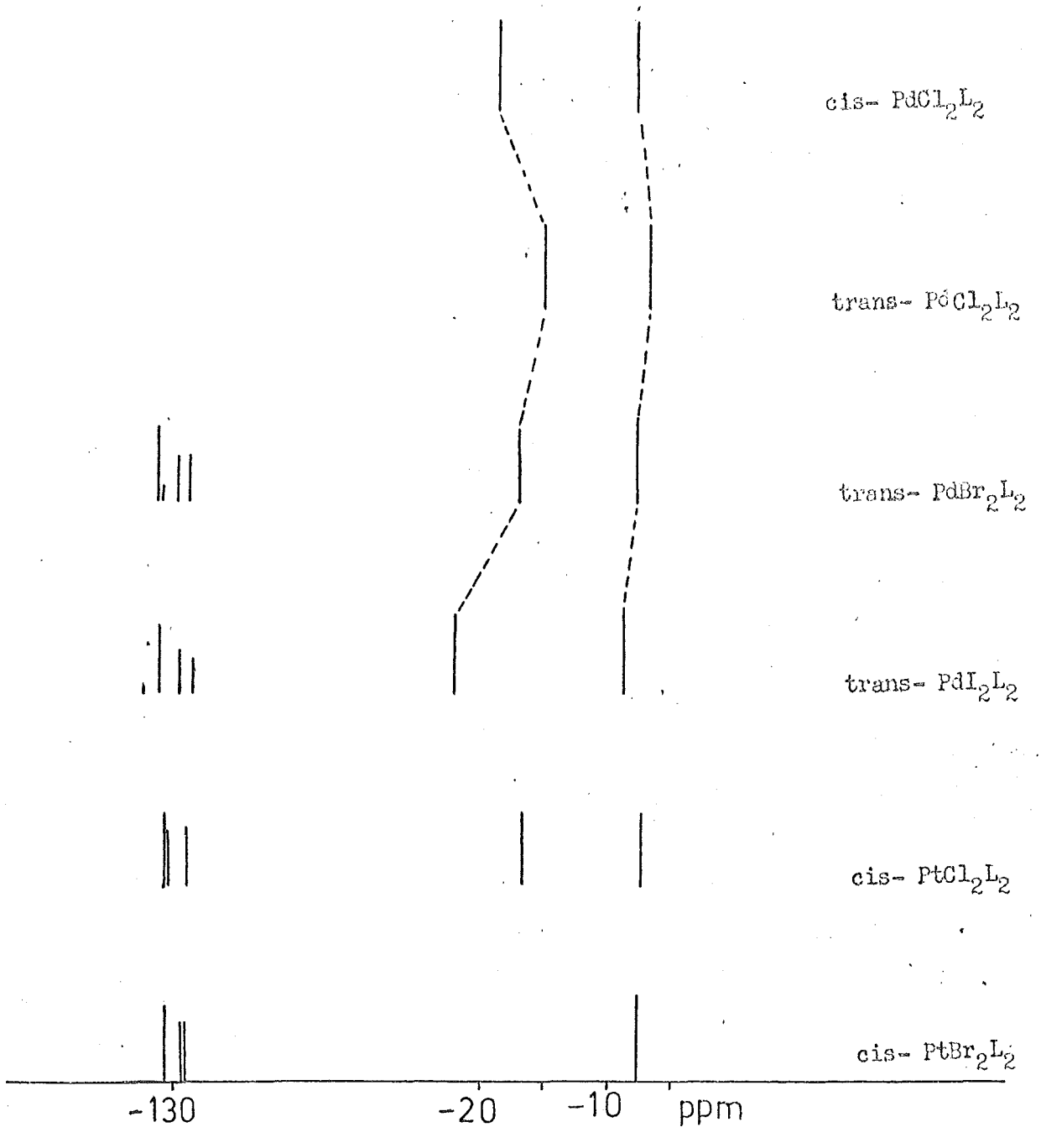
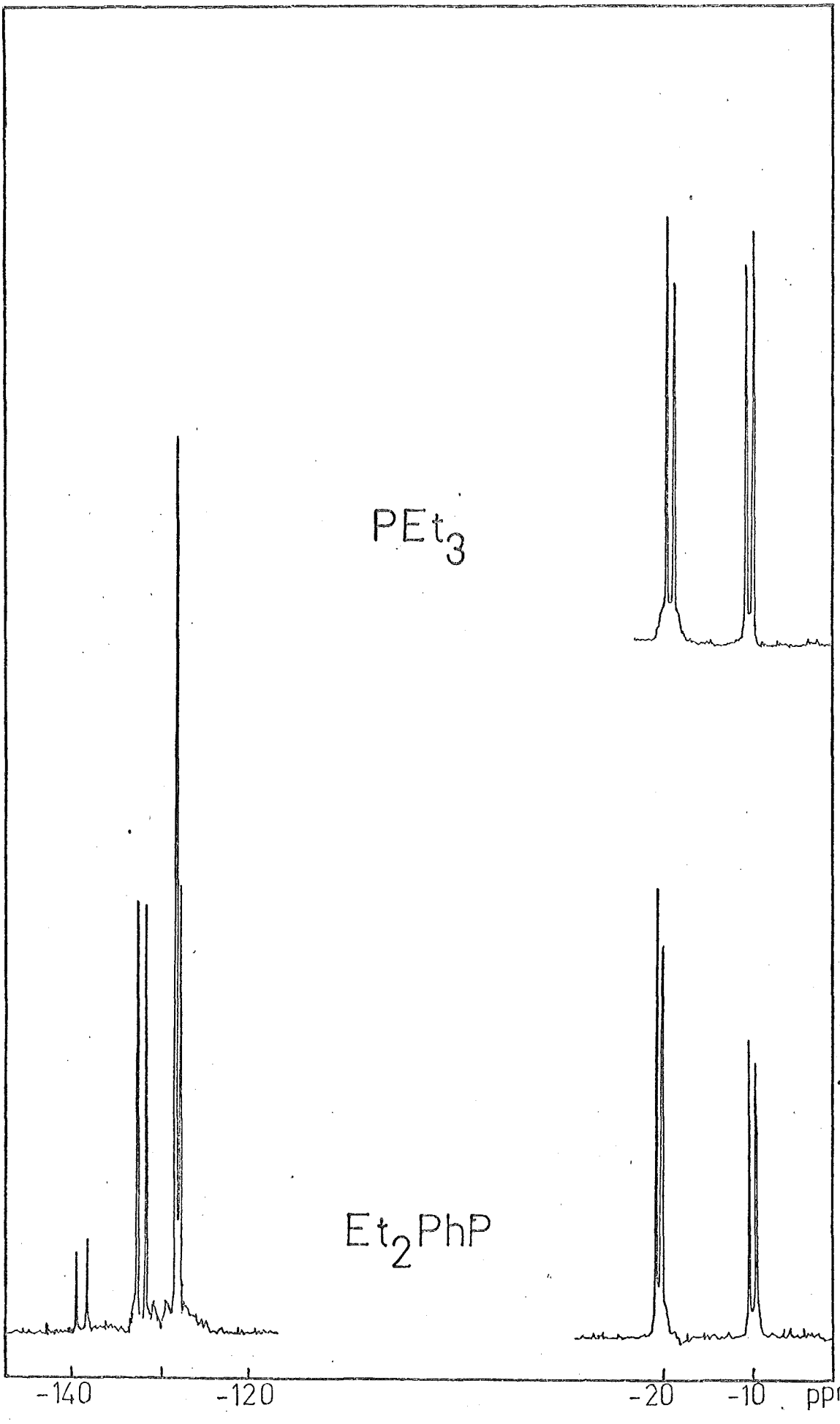


FIGURE 2·18

^{13}C NMR SPECTRA OF PHOSPHINE LIGANDS



in Fig. 2.18.

For both ligands the methyl and methylene multiplets are doublets, which is expected from coupling of the ^{13}C nucleus with ^{31}P. Relevant coupling constants are 14.0Hz ($^{2}J(^{13}C-^{31}P)$) and 13.8Hz ($^{1}J(^{13}C-^{31}P)$) for triethylphosphine, and 15.0Hz ($^{2}J(^{13}C-^{31}P)$ and 12.0Hz ($^{1}J(^{13}C-^{31}P)$) for diethylphenylphosphine. In the phenyl region for the phosphine Et_2PhP there will be four different environments for the carbon atoms. Thus the doublet furtherest downfield at -139.2 ppm ($^{1}J(^{13}C-^{31}P)$=18Hz) may be assigned to the carbon attached to phosphorus, labelled C_1 (Fig. 2.15). The next doublet at -132.5 ppm ($^{2}J(^{13}C-^{31}P)$=18Hz) may be assigned to the ortho-carbon resonance. It has been shown[131] for ^{13}C chemical shifts in monosubstituted benzene derivatives that for o-,m-, and p- carbon atoms the ortho carbon resonance is most shifted from the position of the free benzene resonance, and this empirical observation[131] supports the assignment made above. Conversely the meta-carbon has been shown[131] to be least shifted from the position found for free benzene and hence the assignment is made in the Et_2PhP spectrum to the doublet at -128.4 ppm (one component overlaps with the para-carbon resonance). The coupling constant $^{3}J(^{13}C-^{31}P)$ for the methyl carbon is 6Hz . The remaining single line resonance at -128.5 ppm can therefore be assigned to the para-carbon atom, and this assignment is supported by the singlet nature of this resonance. This may be expected on the basis of the relative remoteness of C_{para} from the phosphorus nucleus.

(d) Assignments for square planar complexes:-

(i) Nickel (II) complexes The ^{13}C NMR spectra of nickel (II) complexes have not been extensively investigated in the present work since, as noted before (p.42), ligand dissociation leads to decomposition of the complexes, at a rate

which increases from chlorine to bromine to iodine. Since the accumulation time for ^{13}C NMR spectra of isotopically unenriched compounds is relatively long this decomposition has limited the study of these nickel complexes by this method. It is notable, however, that both the paramagnetic deshielding phenomenon in Et_2PhP complexes and the broad unstructured nature of the multiplets, as observed for the ^1H NMR spectra (p.42), are again in evidence here, and these can be explained as discussed previously (pp. 42,52).

(ii) Palladium (II) complexes The trans palladium complexes give well-resolved narrow line spectra, with a 1:2:1 triplet for the methylene carbon due to the virtual coupling interaction of the trans phosphorus atoms. The methyl resonance is a singlet and shows no sign of coupling with ^{31}P.

The phenyl resonance in palladium (II) complexes of diethylphenylphosphine is notable for the absence of an absorption corresponding to the C_1 carbon; presumably the relaxation time is too long for this particular nucleus to allow its resonance to be observed. The addition of a small (approximately 50mg) quantity of the complex tris(acetylacetonato)chromium(III) in order to reduce the relaxation times, allows the C_1 resonance to become discernable above the background noise, at least for the bromo and iodo complexes. Apart from C_1 the other three carbon types in the phenyl region can be satisfactorily assigned, analogously to the assignments for the free ligand. The meta and ortho carbons show triplets because of the virtual coupling phenomenon, but the para carbon is a sharply defined singlet and shows no evidence of coupling with ^{31}P, presumably because of its greater distance from the phosphorus nucleus.

FIGURE 2·19

^{13}C NMR SPECTRA OF PALLADIUM(II) COMPLEXES

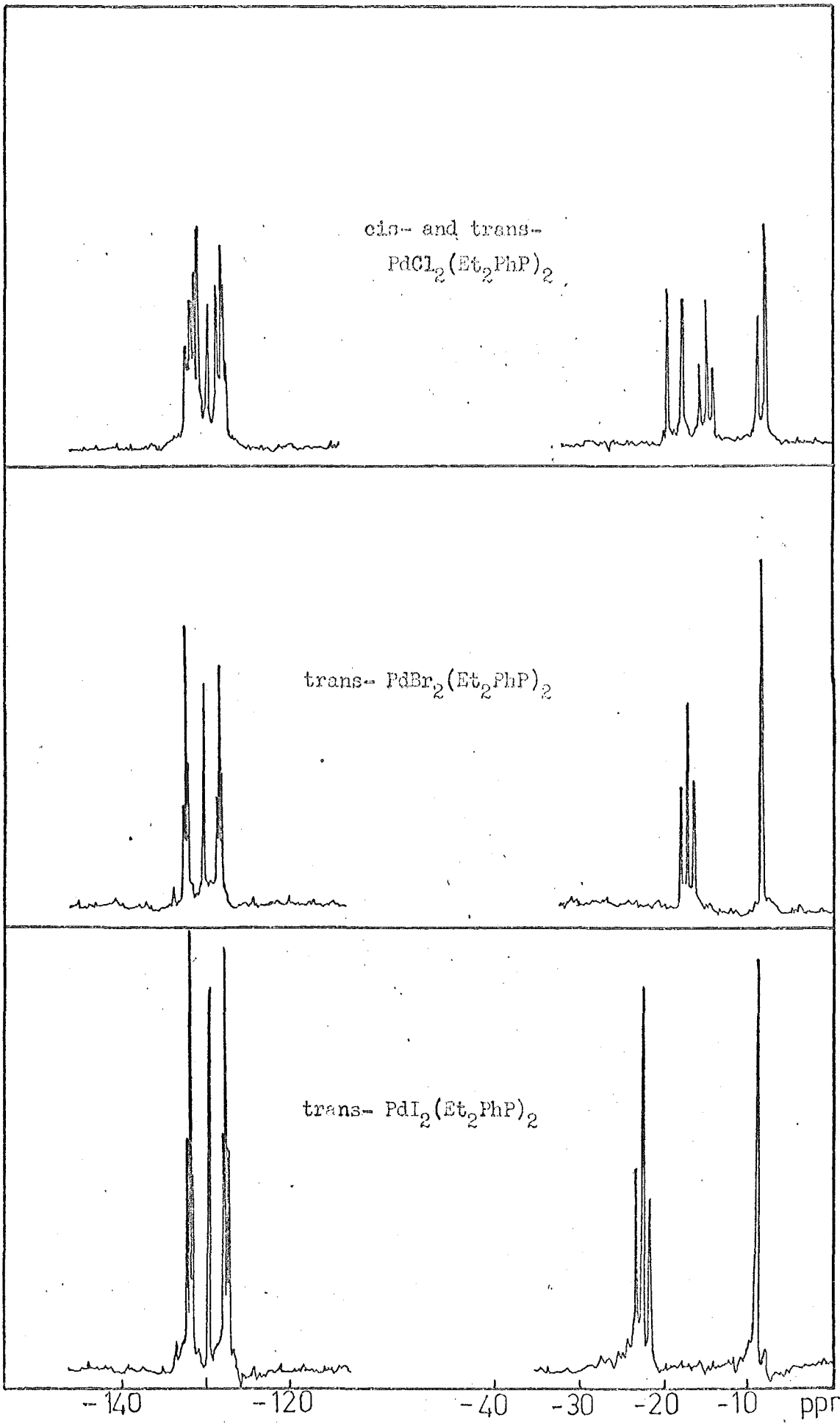


TABLE 2.20

^{13}C NMR spectra of Square Planar Complexes[a]

Compound	methyl	methylene	C_1	C_{ortho}	C_{meta}	C_{para}
trans-$NiCl_2(PEt_3)_2$	-8.26 s	-13.42 s				
trans-$NiCl_2(Et_2PhP)_2$	-11.7 s	-19.5 s	-136.0 s	-135.0 s	-127.6 s	-131.2 s
trans-$NiBr_2(Et_2PhP)_2$	-19.6 s	-32.5 s		-140.9 s	-125.5 s	-134.4 s
trans-$PdCl_2(PEt_3)_2$	- 8.05 s	-13.84 t (26.9)				
trans-$PdBr_2(PEt_3)_2$	- 8.33 s	-15.64 t (27.6)				
trans-$PdI_2(PEt_3)_2$	- 8.89 s	-19.98 t (30.2)				
cis-$PdCl_2(Et_2PhP)_2$	- 8.28 s	-17.69 d (32.4)		(c)		
trans-$PdCl_2(Et_2PhP)_2$	- 7.55 s	-14.20 t (28.6)		(c)		
trans-$PdBr_2(Et_2PhP)_2$	- 8.22 s	-16.52 t (29.2)	-131.44 s (b)	-132.03 t (11.6)	-128.22 t (9.6)	-129.97 s
trans-$PdI_2(Et_2PhP)_2$	- 8.92 s	-21.84 t (30.8)	-133.76 s (b)	-132.04 t (10.4)	-127.94 t (9.8)	-129.76 s
trans-$PtCl_2(PEt_3)_2$	- 8.0 s	-12.8 t (32.0)				
trans-$PtI_2(PEt_3)_2$	- 8.5 s	-18.2 t (36.0)				
cis-$PtCl_2(PEt_3)_2$	- 8.5 s	-16.8 (44.0)(d)				
cis-$PtCl_2(Et_2PhP)_2$	- 8.1 s	-16.8 (44.0)(d)		-131.6 t (10.0)	-128.5 t (10.0)	-131.0 s
cis-$PtBr_2(Et_2PhP)_2$[e]	- 8.4 s			-131.4 t (8.0)	-128.2 s	-128.7 s
$Pt_2Cl_4(PEt_3)_2$	- 7.5s - 7.7 s	-14.1 d (42.0) -15.6 d (40.0)				

(cont...)

TABLE 2.20 (continued)

^{13}C NMR spectra of Square Planar Complexes [a]

Compound	methyl	methylene	methoxy	C_{ortho}	C_{meta}
$Pt_2Br_4(PEt_3)_2$	- 7.9 s - 8.0 s	-16.0 d (40.0) -17.0 d (40.0)			
$Pt_2I_4(PEt_3)_2$	- 8.32 s	-18.24 d (40.0)			
$PdCl_2((p\text{-}MeOPh)Et_2P)_2$					
cis	- 8.6 s	-18.2 d (34.0)	-55.45 s [f]		
				-133.7 t (12.0)	-114.1 t (10.0)
trans	- 7.9 s	-14.8 t (28.0)	-55.20 s		

(a) chemical shifts in ppm downfield from TMS coupling constants (HZ) in parentheses

(b) observed on addition of $Cr(acac)_3$

(c) complex multiplet. Not possible to assign cis and trans components

(d) "filled-in" doublet (see text)

(e) poor resolution

(f) Not possible to decide the contributions of each isomer to the C_{ortho} and C_{meta} resonance multiplets

(g) s = singlet; d = doublet ; t = triplet

The presence of cis and trans isomers of $PdCl_2(Et_2PhP)_2$ in equilibrium in chloroform solution is clearly observed from the spectrum of this complex. The methyl and methylene regions can be interpreted quite simply since for the methylene a 1:1 doublet downfield of a 1:2:1 triplet is observed, while the methyl region shows two singlets (Figure 2.19). The methyl carbon resonance with the larger chemical shift relative to TMS is assigned to the cis isomer; this was done on the basis of integration of the methyl resonance and comparison with the integrated intensities of the two types of methylene resonances. Integration is expected to be valid in this case since relaxation times for analogous resonances in these two isomers may be expected to be similar. The 1:1 doublet methylene resonance is assigned to the cis isomer on the basis of the lack of virtual coupling producing a doublet in cis isomers (see p.56) and similarly the 1:2:1 triplet for the other methylene carbon is assigned to the trans isomer since virtual coupling is present in this case. It is of interest that the doublet in the cis isomer spectrum is of true 1:1 intensity; hence by the earlier arguments[74](p.56) Jpp should be very close to zero in this case.

The ^{13}C spectrum of $PdCl_2$ ($(p\text{-}MeOPh)Et_2P)_2$ is readily assigned in the ethyl resonance region (see Table 2.20). The spectrum shows evidence for the existence of both cis and trans isomers in solution, since a doublet and a triplet are observed in the methylene region and two singlets in the methyl region. This situation is therefore analogous to that discussed above for the unsubstituted Et_2PhP complex. The methoxy carbon is also a doublet. No attempt was made to separate the isomers and integration shows that the trans/cis ratio is approximately 3:1 at 30°. This is the same as the ratio of trans/cis isomers in $PdCl_2(Et_2PhP)_2$.

(iii) Platinum (II) complexes The spin system in the platinum (II) complexes is different from the palladium case since ^{195}Pt (natural abundance 33.8%) has a spin of $\frac{1}{2}$. Just how this affects the spectra cannot be ascertained accurately however, because of the poor resolution and quality of the spectra obtained. In the case of cis-$PtCl_2(Et_2PhP)_2$ a "filled-in" doublet (see pp. 55, 56) is clearly evident for the methylene multiplet and this suggests, following the ideas[74] discussed earlier (p. 56), that Jpp is not zero for this complex. If the value of this coupling constant was zero a true 1:1 doublet should be observed. That this is not the case may reflect the lack of true C_{2v} symmetry for these complexes.[37] i.e. the P-Pt-P bond angle is no longer 90°.

(e) Trends in the spectra of square planar mononuclear complexes:-

The ^{13}C NMR spectra of mononuclear square planar complexes show a number of trends within and between the various series (Table 2.20) and these will now be considered.

The deshielding of the methylene resonance multiplet in trans complexes increases with change in halogen from chlorine to bromine to iodine, identical to the deshielding discussed previously for the ^{1}H NMR spectra (Section 2.2.2). Thus this effect may be explained in a similar way as before (pp. 44-46) i.e. either non-bonded interaction of the halogen lone pairs on the organic groups, or electron drift from the organic groups to the metal ion, as a consequence of either $M_{d\pi} \longrightarrow X_{d\pi}$ bond formation or polarisation effects of the halogeno-ligands. The π -bonding explanation is perhaps supported by results found for zinc complexes (see later discussion), but any proposals must be regarded with caution, since other factors such as the magnetic

anisotropies of the metal ion, or metal-ligand bonds (pp. 46,47), may also be important.

Contrary to the proton case the methyl carbons also show a deshielding with halogen change in the same order as above (but the effect is less than it is for the methylene resonances, see Table 2.20). For the proton spectra (p. 48) the observed small shielding was discussed in terms of intramolecular non-bonded interactions with the halogeno-ligands. The opposite trend in the ^{13}C spectra may be related to the fact that an intramolecular interaction with the halogens will be less for the methyl carbon atoms since these are somewhat protected by the attached protons. This protection would thus allow the intermolecular electronic effects invoked above for the methylene case to become dominant, hence leading to the observation of deshielding.

The coupling constant, $^{1}J(^{13}C-^{31}P)$ for the 1:2:1 triplet methylene resonance in palladium (II) complexes varies from 26.9 Hz (chloro-complex) to 27.6Hz (bromo-complex) and 30.2Hz (iodo-complex) in the PEt_3 complexes and a similar order is observed for the Et_2PhP complexes. The uncertainty in measurement is considered to be $\pm$ 0.2Hz and hence the above trend is significant. The increase in coupling constant may reflect an increase in phosphorus-carbon interaction.

A comparison of the chemical shifts of the methylene multiplets in cis- and trans- $PdCl_2(Et_2PhP)_2$ (Table 2.20 and Fig. 2.19) shows that the deshielding is greater for this cis complex. Again, as discussed for a similar observation in the proton spectra of these isomers (p. 43), this can be attributed to a stronger metal-phosphorus bond in the cis complex. The greater involvement of the phosphorus lone pair in the cis case will draw

TABLE 2.21

^{13}C NMR spectra of zinc (II) complexes[a]

Compound	methyl	methylene	C_1	C_{ortho}	C_{meta}	C_{para}
$ZnI_2(Et_2PhP)_2$	- 7.72 s	-15.23 t (21.0)	-133.19 s	-131.73 s	-129.00 s	-130.56 s
$ZnCl_2(PEt_3)_2$	- 7.91 s	-13.72 [b]				
$ZnBr_2(PEt_3)_2$	- 7.93 s	-13.80 t (16.8)				
$ZnI_2(PEt_3)_2$	- 7.96 s	-13.89 t (20.6)				

(a) s = singlet; t = triplet

chemical shifts in ppm downfield from TMS

coupling constants (Hz) in parentheses

(b) broad and no structure resolved (see text and Fig. 2.20)

fractionally more charge from the organic groups, hence leading to an increased deshielding, as observed.

It is noticeable (see Table 2.20) that the extent of the methylene carbon deshielding in platinum (II) complexes is now less than that for analogous palladium (II) complexes. This is the opposite of the situation found for the proton NMR spectra (Table 2.14), where the result was construed as supporting the $M_{d\pi} \longrightarrow X_{d\pi}$ bonding hypothesis on the basis of the greater π-bonding ability expected for platinum as compared with palladium. The reason for the opposite trend in the ^{13}C NMR spectra is not obvious, but the result does cast doubt on the validity of the π-bonding trends advanced above to explain the situation found for the proton spectra.

(f) Spectra of binuclear platinum (II) complexes:-

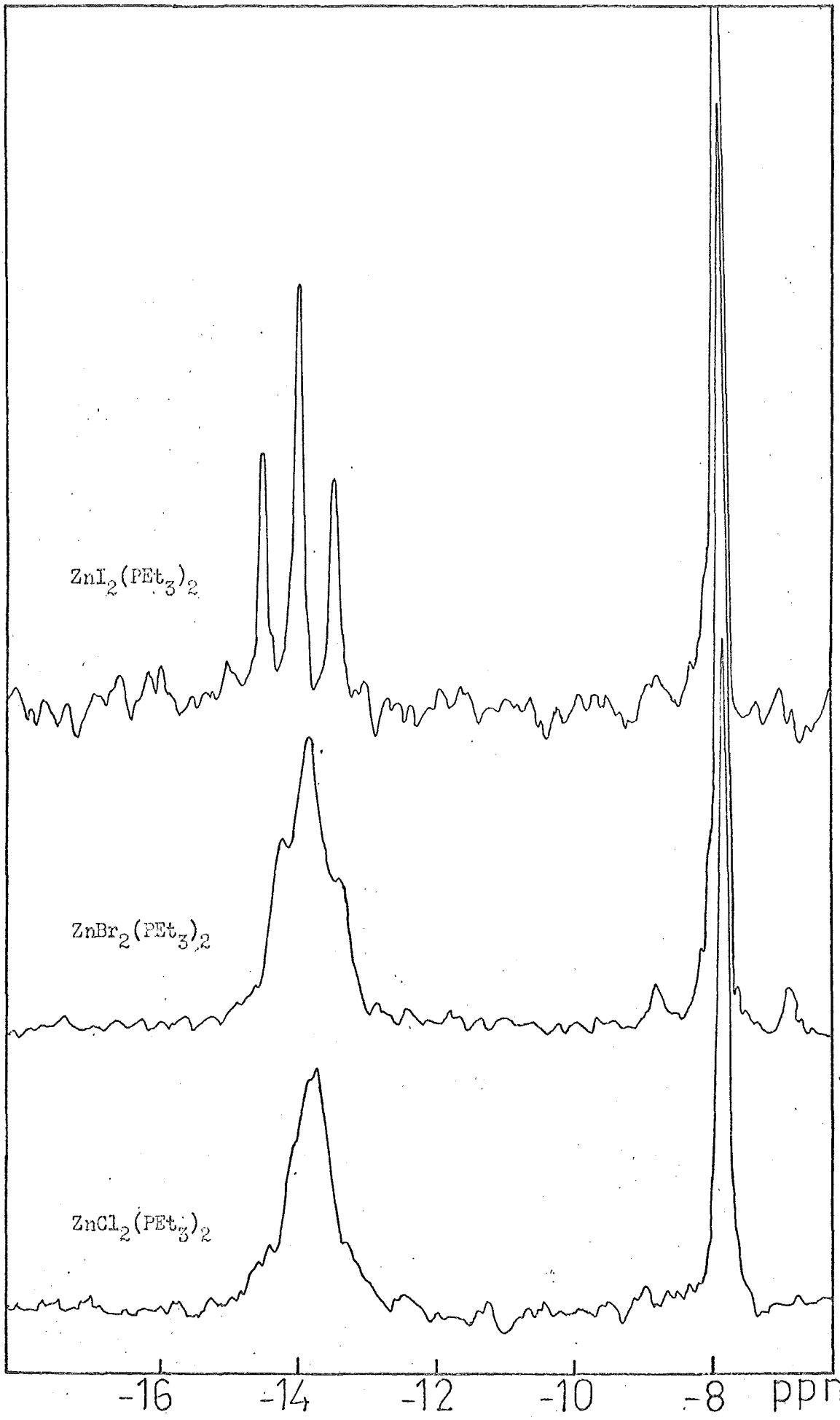
The ^{13}C NMR spectra of $Pt_2X_4(PEt_3)_2$ (X = Cl,Br) complexes show two singlet methyl resonances and two doublet methylene resonances, each pair of resonances being in the ratio 3:1, with the more intense resonance at higher field. It is probable that the resonance pairs originate from the presence of two different phosphine environments in the complexes. The doublet resonances are expected on the basis of lack of virtually coupled phosphorus nuclei (see p. 56). The iodo complex does not show any evidence for different phosphine environments which is perhaps surprising in view of the probability of largest steric interactions in this case as compared with chloro and bromo complexes.

(g) Spectra of tetrahedral zinc (II) complexes:-

The ^{13}C NMR spectra of tetrahedral zinc (II) complexes are given in Table 2.21 and Fig. 2.20. The resonances are broad and multiplet structure is well defined only for the iodo complex

FIGURE 2·20

^{13}C NMR SPECTRA OF ZINC(II) COMPLEXES



at room temperature (see Fig. 2.20). This is a similar situation to that observed for the ^{1}H NMR spectra of these complexes and the explanation in terms of ligand dissociation in solution (p. 52) should be equally valid here.

An approximate 1:2:1 triplet is observed (at least in the iodo complex, see Fig. 2.20) for the methylene resonance, and this is further evidence for the differing total spin systems in the ^{13}C NMR and ^{1}H NMR spectra of metal phosphine complexes. In these tetrahedral zinc (II) complexes the value of Jpp is expected to lie within the range of strong virtual coupling expected for trans phosphines and zero virtual coupling expected for cis phosphines, in square planar compounds. As discussed earlier this situation will probably give rise to a triplet, as is observed. In contrast, the ^{1}H NMR spectra of the zinc (II) complexes show doublet resonances through coupling with phosphorus and this again illustrates that the different total spin systems for ^{1}H and ^{13}C NMR spectra may give rise to different multiplicities.

For both methyl and methylene resonances, the variation in chemical shift with change in halogen is slight (Table 2.21). Overall this near constancy can be taken, as discussed for the proton case, to imply that the magnetic interaction of halogen lone pairs is probably not the determining factor in the observation or nonobservation of deshielding with change in halogen. However, as noted earlier (p. 53) this is not altogether certain because the zinc complexes are pseudo-tetrahedral and the transition metal complexes square planar, and hence intramolecular non-bonded interactions may be less severe for the less stereochemically constrained environment.

2.2.4 Phosphorus-31 Nuclear Magnetic Resonance Spectra

The ^{31}P NMR spectra of a number of palladium (II) and

platinum (II) halogeno-phosphine complexes have been obtained in this work. The chemical shift data, and coupling constants (where relevant) for the complexes are given in Table 2.22 and some representative spectra are sketched in Fig. 2.21. There are a number of inherent limitations in the technique of ^{31}P NMR spectroscopy and these have reduced the number of complexes open to study by ^{31}P NMR in the present work. The most important of these limitations is the very low NMR sensitivity of the phosphorus-31 nucleus (6.63% of the sensitivity of the proton[132]). This means that the concentration of ^{31}P nuclei required to obtain a signal comparable with that obtained from ^{1}H NMR spectra is much larger. Further in these bis (phosphine) complexes there are only two ^{31}P nuclei per molecule compared with either twelve (PEt_3) or twenty (Et_2PhP) ^{1}H nuclei. Again, therefore, a greater concentration of the complex is required for the observation of ^{31}P resonances. The use of a computer of average transients (CAT) is possible but the scanning width of the CAT used in this work was not sufficient to extend the scan as far as the ^{195}Pt-^{31}P satellites in platinum (II) complexes, and hence this technique was of limited applicability. The final limitation is the solubility of the complexes. Chloroform is generally employed as solvent but a number of complexes selected for study in the present work had only limited solubility in $CHCl_3$ and this precluded the obtaining of satisfactory spectra for these compounds.

Discussion of Results:-

The data given in Table 2.22 shows a number of features of interest. The palladium (II) complexes have spectra which show only one absorption peak. This implies that the phosphorus atoms are equivalent in these compounds. For platinum (II) the ^{31}P NMR spectrum is a triplet; the central component arises from molecules

TABLE 2.22

^{31}P NMR Spectra of palladium(II) and platinum(II) halogeno-phosphine complexes [a]

Compound	X	Chemical shift	$^1J(^{195}Pt - ^{31}P)$
PEt_3		+ 20.1 [c]	
Et_2PhP		+ 17.6 [c]	
trans-$PdCl_2(PEt_3)_2$		- 17.6	
trans-$PdBr_2(PEt_3)_2$		- 15.2	
trans-$PdI_2(PEt_3)_2$		- 8.9	
trans-$PdCl_2(Et_2PhP)_2$		- 15.6	
trans-$PdBr_2(Et_2PhP)_2$		- 11.2	
trans-$PdI_2(Et_2PhP)_2$		- 4.7	
cis-$PtCl_2(Et_2PhP)_2$		- 3.1	3640
cis-$PtBr_2(Et_2PhP)_2$		- 2.4	3580
cis-$PtCl_2(PEt_3)_2$		- 9.6	3520
trans-$PtCl_2(PEt_3)_2$		-11.8	2400
trans-$PtBr_2(PEt_3)_2$		- 7.4	
trans-$PtX_2(Bu_3P)_2$ [b]	Cl	- 4.9	2380
	Br	0.0	2334
	I	+ 7.9	2220
cis- $PtX_2(Bu_3P)_2$ [b]	Cl	- 1.4	3508
	Br	- 0.8	3479
	I	+ 1.1	3372

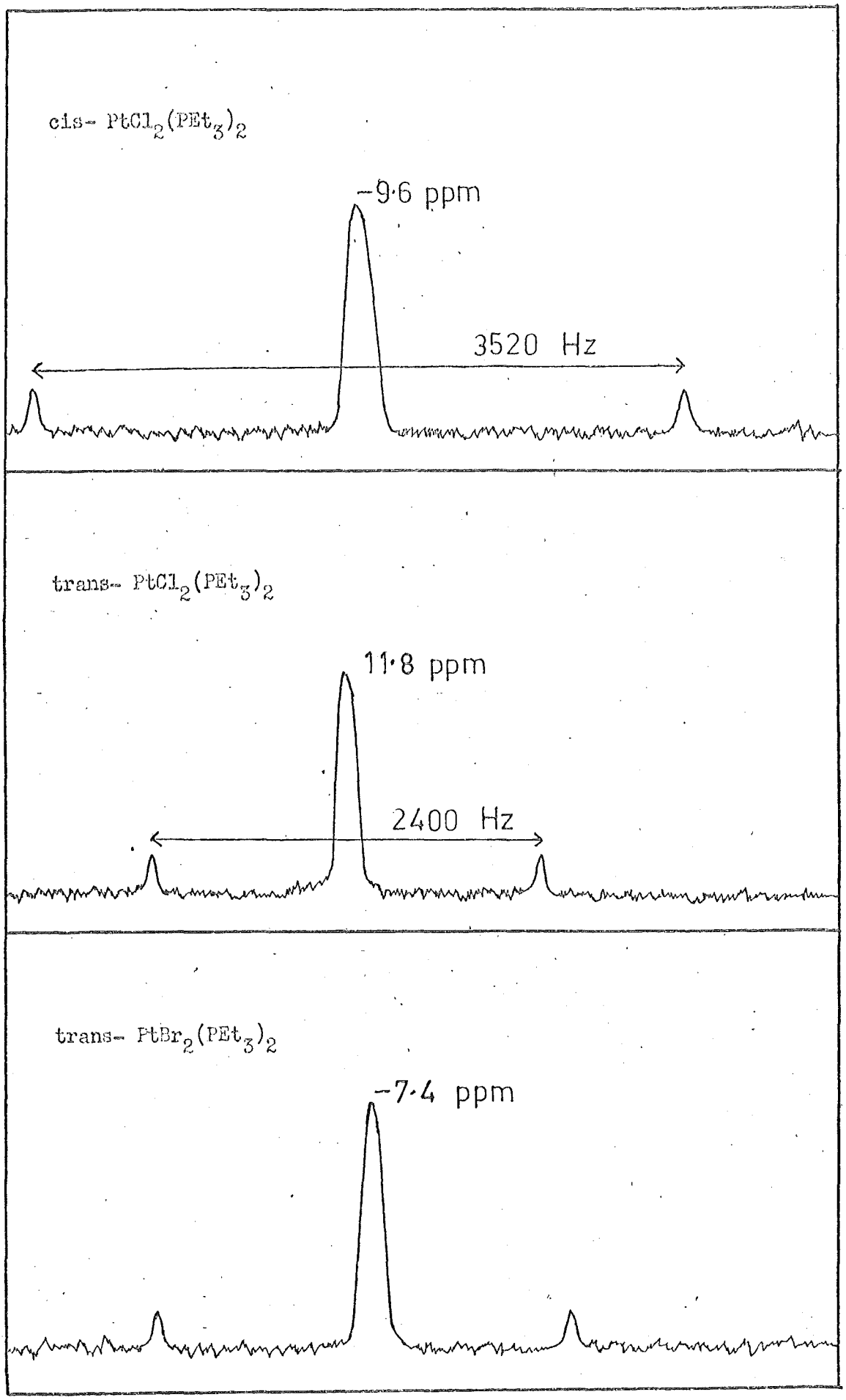
(a) chemical shifts in ppm relative to 85% H_3PO_4
coupling constants in Hz

(b) Data from ref. 33

(c) Data from ref. 130

FIGURE 2·21

^{31}P NMR SPECTRA OF PLATINUM(II) COMPLEXES



containing platinum nuclei with zero spin, and the two outer satellite components arise from molecules containing the ^{195}Pt nucleus which has a spin quantum number of $\frac{1}{2}$.

(a) Chemical shift trends:-

For both palladium (II) and platinum (II) complexes the trend in chemical shift with change in halogen in the order Cl,Br,I is to higher field. This reflects an increasing shielding of the phosphorus nuclei with halogen change, and the probable reason for this is a drift of electrons from the organic groups on phosphorus into the metal-phosphorus bond. A possible reason for this drift is that the influence of $M_{d\pi} \longrightarrow X_{d\pi}$ bonding in the complexes (which would increase in the order Cl,Br,I) will induce an increasing component of positive charge on the metal ion and charge draw-off from the organic groups will occur to compensate for this. This explanation is supported by results found by Pidcock et al.[33] (given in Table 2.22) for cis and trans platinum (II) complexes, where the shielding with halogen change is greater for the trans complexes. In the cis case the extent of possible $Pt_{d\pi} \longrightarrow X_{d\pi}$ bonding may be expected to be less than in the trans stereochemistry because the halogeno-ligands are competing for suitable metal $d\pi$ orbitals with the phosphorus atoms in the cis case, and phosphorus is considered to be a better $d\pi$ acceptor.

Upon coordination there is a large downfield chemical shift for the phosphorus resonances in both palladium (II) and platinum (II) complexes. This may be expected on the basis of the donation of the phosphorus lone pair of electrons to the metal ion and a consequent deshielding of the phosphorus nuclei.[133] The coordination chemical shift is less for cis platinum complexes as compared with the trans analogues. This might imply a greater electron density in the metal-phosphorus bond in the cis case, and this is consistent

with the results of Chatt and Wilkins[30,31] who showed that the metal-phosphorus bond is stronger in the cis complexes.

(b) (^{195}Pt-^{31}P) coupling constants in platinum (II) complexes:-

The interpretation of trends in ^{195}Pt-^{31}P coupling constants in platinum (II) halogeno-phosphine complexes has been the subject of considerable debate in recent years[134] (see Chapter 1, pp. 10,11). Pidcock and co-workers[33,34,38] have taken the view that the results can be interpreted in terms of strong platinum-phosphorus σ bonding, with a negligible component of Pt-P $d\pi - d\pi$ bonding, whereas Grim et al.[39-41] have discussed similar results in terms of a substantial amount of $M_{d\pi} \longrightarrow P_{d\pi}$ bonding.

The trends which may be noted in Table 2.22 are that change in halogen in the order Cl,Br,I for otherwise analogous complexes results in a small but significant decrease in the value of $^{1}J(^{195}Pt-^{31}P)$, and a comparison between cis and trans isomers shows that J is approximately 1.5 times larger for the cis complex. These trends are shown more clearly in the extended data of Pidcock et al.[33], given in Table 2.22

Decreases in coupling constants may be taken to imply a decrease in interaction between the bonded atoms, and hence a lessened bond strength. This may be expected for the comparison between cis and trans complexes, but in the case of the decrease in J with change in halogen the trend in bond strength is the opposite of that deduced from chemical shift measurements. This may simply be a reflection of the present state of theoretical understanding of both ^{31}P chemical shifts and spin-spin coupling interactions. The interpretations of both of these phenomena are subjects of some debate.[134]

2.2.5 Electronic Absorption Spectra

(a) Square planar mononuclear complexes:-

The compounds studied by electronic absorption spectroscopy were of the form trans - $MX_2(PEt_3)_2$ (M = Ni,Pd,Pt ; X = Cl,Br,I) and cis - $PtX_2(PEt_3)_2$ (X = Cl,Br,I). The spectra were recorded in methanol or ethanol solution.

The spectra of the nickel complexes have been discussed before by Coussmaker et al.,[115] and similar complexes with tripropylphosphine and tricyclohexylphosphine ligands have been studied by Giacometti and Turco.[49] Jorgensen[135] has considered some unpublished results of Canadine[97] on palladium halogeno-complexes with an unspecified tertiary phosphine, PR_3. Other electronic spectral data has been limited to scattered compounds in connection with other lines of work.[44] Gray and Ballhausen[136] have discussed a molecular orbital theory for square planar complexes of the form $[MX_4]^{2-}$ (M = Ni,Pd,Pt) and this work is of assistance to the present study in assigning ligand field and charge transfer bands.

The spectral bands and assignments made are given in Table 2.23 and the spectra of the nickel complexes are shown in Fig. 2.22 as representative examples.

There are in general three distinct regions of absorption in the U.V. - visible spectra of these compounds. The two regions at higher energy have extinction coefficients considerably greater than 10^3 and hence can be assigned to charge transfer transitions between the ligands and the metal ion. The free ligand spectrum has no absorptions in the region 220 - 1000 nm.

The third absorption region is a single broad band at lower energy ($>$400 nm) which has an extinction coefficient of the order

TABLE 2.23

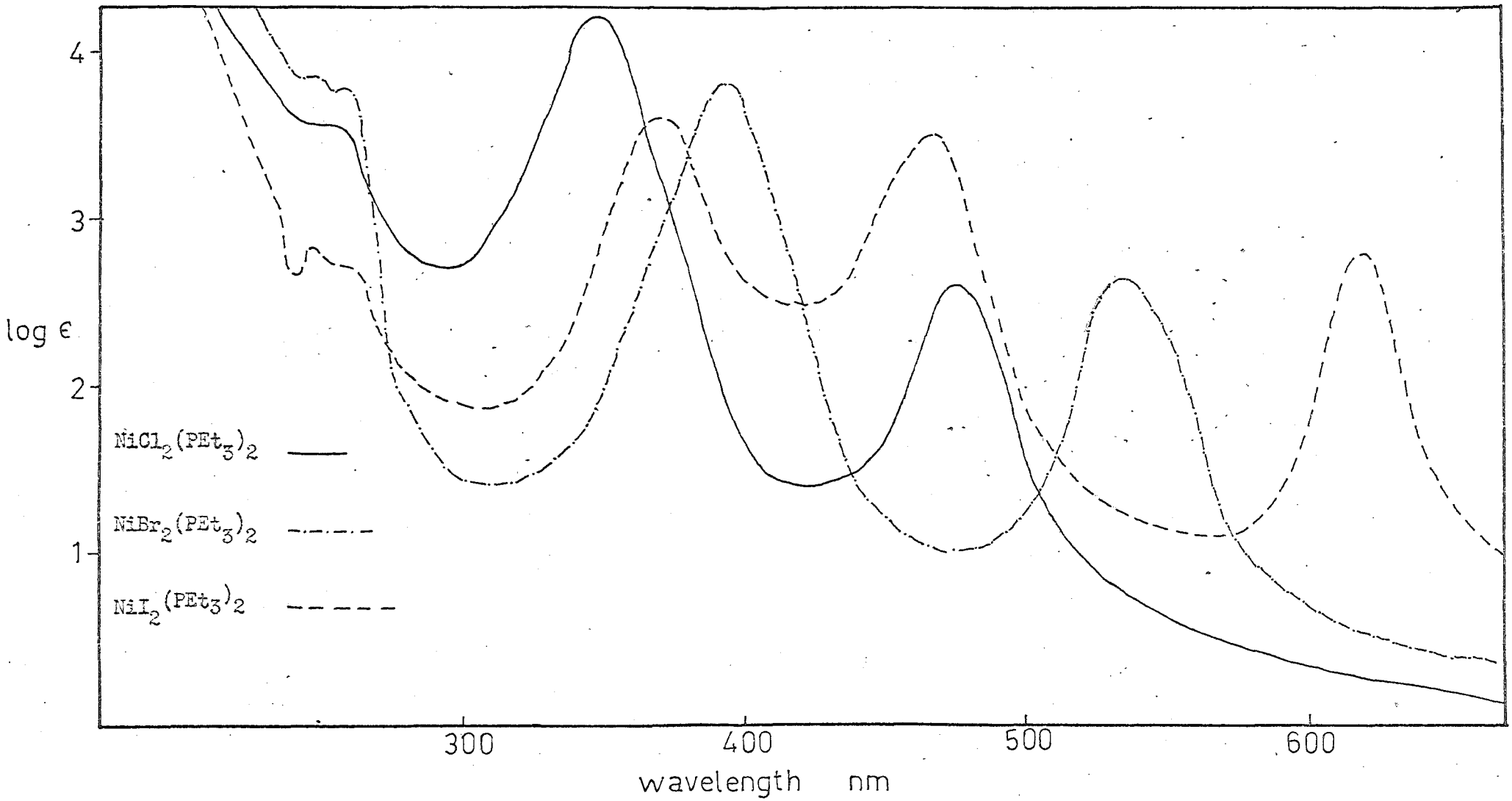
Electronic spectra of mononuclear square planar complexes[a]

Compound	Band Assignment: ligand field (see text)		$X_{nb} \longrightarrow M$ (halogen → metal)		$P_{nb} \longrightarrow M$ (phosphine — metal)		Other	
$NiCl_2(PEt_3)_2$	487	(380)	369	(16,000)	277 sh	(3,300)		
$NiBr_2(PEt_3)_2$	539	(360)	398	(8,250)	277 sh 282 sh	(7,800) (6,000)		
$NiI_2(PEt_3)_2$	616	(450)	372 456	(4,120) (2,490)	272 286 sh	(2,260) (2,000)		
$PdCl_2(PEt_3)_2$			324	(13,400)	229 237 sh	(13,400) (9,500)		
$PdBr_2(PEt_3)_2$			347	(8,600)	229 sh	(26,000)	250	(13,000)
$PdI_2(PEt_3)_2$			398 335	(3,700) (3,000)	233 248	(18,000) (27,000)	268 sh 294	(14,000) (12,600)
trans-$PtCl_2(PEt_3)_2$			267	(4,700)	233 248	(5,300) (6,100)		
trans-$PtBr_2(PEt_3)_2$			281	(4,700)	233 sh 253	(7,700) (4,100)		
trans-$PtI_2(PEt_3)_2$			284 336	(7,200) (2,200)	252 sh	(11,600)		
cis-$PtCl_2(PEt_3)_2$			319	(430)	236 sh	(8,600)	262 sh	(2,500)
cis-$PtBr_2(PEt_3)_2$					229 sh	(15,700)		
cis-$PtI_2(PEt_3)_2$			285 335	(4,700) (2,200)				

(a) wavelengths in nanometres extinction coefficients in parentheses
sh = shoulder

FIGURE 2·22

ELECTRONIC SPECTRA OF $NiX_2(PEt_3)_2$ COMPLEXES



of 10^2. This band is observed only in the spectra of the nickel complexes, and possibly for $PdI_2(PEt_3)_2$ (see below). In the palladium and platinum compounds the proximity of an intense charge transfer band masks the weaker ligand field transitions which would be expected to occur at higher energy than in the nickel case. For the nickel complexes the weak band shows a consistent shift to lower energy in the order chlorine, bromine, iodine. This order is also that of weakening ligand field and hence the bands may be assigned to ligand field transitions. The relatively high extinction coefficients arise because the broad band can comprise up to three overlapping bands corresponding to the three possible transitions in square planar MX_2L_2 complexes with the d^8 electron configuration. For trans compounds these have the form $A_g \xrightarrow{(1)} B_{1g}$; $A_g \xrightarrow{(1)} A_g^{(2)}$; and $A_g \xrightarrow{(1)} B_{2g}$, B_{3g} (D_{2h} symmetry). For cis complexes (C_{2v} symmetry) the labels are $A_1 \xrightarrow{(1)} A_2$; $A_1 \xrightarrow{(1)} A_1^{(2)}$; and $A_1 \xrightarrow{(1)} B_1, B_2$.

The band in the spectrum of $PdI_2(PEt_3)_2$ at 398nm (ϵ = 3700) is probably a component of the lowest energy charge transfer transition, although for $PdI_2(PR_3)_2$ Jorgensen[135] has tentatively assigned it to a ligand field band. This seems unlikely however since the extinction coefficient is relatively very high, although intensity stealing from the lowest energy charge transfer absorption might be invoked to account for this.

The two regions of charge transfer absorption in the spectra of these complexes can be assigned to transitions involving in the one case the phosphine ligand, and in the other the halogeno-ligand. Thus the rather invariant band around 275nm for the nickel complexes and 230nm for the palladium and platinum compounds can be assigned to a phosphorus-metal charge transfer transition. The other region of absorption is at lower energy but

TABLE 2.24

Electronic spectra of binuclear complexes[a]

Compound	Ligand field (see text)	Band Assignment $X_{nb} \longrightarrow M$ (halogen → metal)	$P_{nb} \longrightarrow M$ (phosphine — metal)	Other
$Pd_2Cl_4(PEt_3)_2$		364 (1,860)	225 (31,000) 258 sh (3,850)	
$Pd_2Br_4(PEt_3)_2$		380 (1,780)	225 (39,000) 249 sh (29,000)	
$Pd_2I_4(PEt_3)_2$		349 (12,600) 452 sh (2,000)	233 (33,000)	284 (20,000)
$Pt_2Cl_4(PEt_3)_2$	445 (40) 355 (360)	319 (710)	221 (16,700) 246 sh (3,600)	272 (1,100)
$Pt_2Br_4(PEt_3)_2$	475 (30) 385 sh (240)	339 (830)	251 (4,300)	284 (1,100)
$Pt_2I_4(PEt_3)_2$	509 (200)	388 (3,200)		282 sh (5,500) 305 sh (4,600)

(a) wavelengths in nanometres
extinction coefficients in parentheses
sh = shoulder

still the extinction coefficient is high. This band varies markedly with change of halogen and, further, the band falls in energy as the halogeno-ligand changes in the order of decreasing electron affinity, i.e. chlorine to bromine to iodine. Thus the band may be assigned to a halogen to metal charge transfer transition, $X_{nb} \rightarrow M$, where X_{nb} represents non-bonding electrons on the halogeno-ligand. This transition is therefore of the metal reduction type. In the case of the iodo complexes the halogen $\rightarrow$ metal charge transfer transition is generally split into two components (see Table 2.23).

(b) Spectra of binuclear complexes:-

The electronic absorption spectra of the binuclear complexes of form $Pd_2X_4(PEt_3)_2$ and $Pt_2X_4(PEt_3)_2$ (X = Cl,Br,I), have been obtained and are assigned as shown in Table 2.24. The spectra were run in methanol where possible but the low solubility of $Pt_2Br_4(PEt_3)_2$ and $Pt_2I_4(PEt_3)_2$ in methanol necessitated the use of chloroform as solvent for these complexes.

The spectral assignments are analogous to those discussed in (a) above for mononuclear complexes. The ligand field bands can be observed for the platinum complexes but are masked in the palladium case. The charge transfer transitions are assigned to phosphorus-metal (higher energy) and halogen to metal (lower energy) transitions, as for the mononuclear compounds.

(c) Spectra of tetrahedral cobalt (II) complexes:-

The complexes are of the form $CoX_2(PEt_3)_2$, (X = Cl,Br,I). The ligand field bands in these spectra represent the $^4A_2 \rightarrow {}^4T$, transition[88] in distorted tetrahedral (C_{2v}) symmetry and it can be seen from Table 2.25 that the band is split to some extent.[87] This could arise from distortions from tetrahedral symmetry[88] or

TABLE 2.25

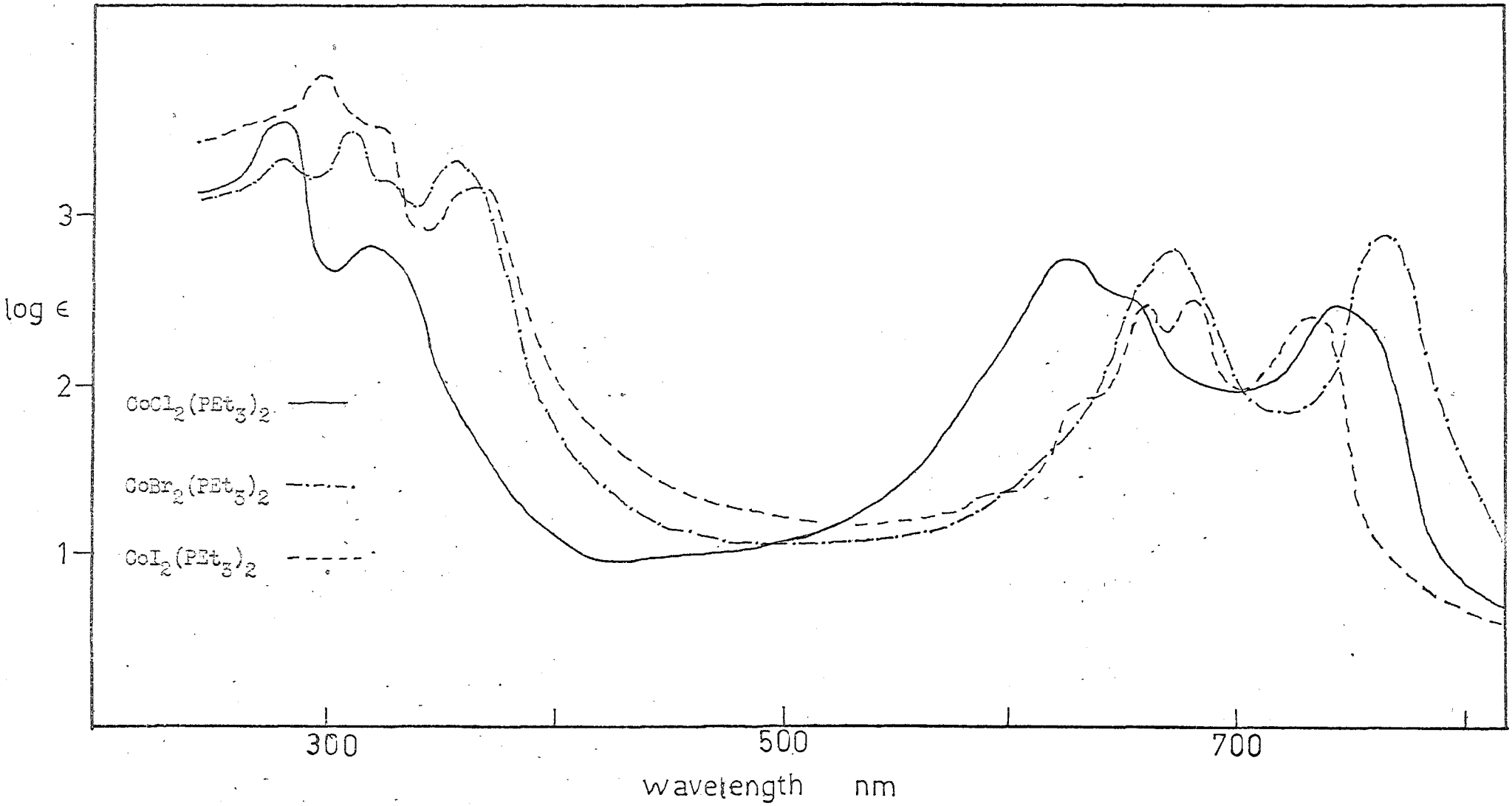
Electronic Spectra of tetrahedral cobalt(II) complexes [a]

Compound	Band Assignment: ligand field $^4A_2 \longrightarrow {}^4T_1$		$X_{nb} \longrightarrow M$ halogen → metal		$P_{nb} \longrightarrow M$ (phosphine — metal)	
$CoCl_2(PEt_3)_2$	734	(300)				
	626 sh	(100)	319	(750)	284	(2,000)
	608	(400)				
$CoBr_2(PEt_3)_2$	748	(600)	341 sh	(1,500)		
	652	(700)	313 sh	(2,000)	283	(1,600)
			300	(3,000)		
$CoI_2(PEt_3)_2$	720	(150)				
	664	(200)				
	635	(250)	334	(800)	293	(1,500)
	618	(150)	312 sh	(1,000)		
	583 sh	(100)				

(a) wavelengths in nanometres
extinction coefficients contained in parentheses
sh = shoulder

FIGURE 2·23

ELECTRONIC SPECTRA OF TETRAHEDRAL $CoX_2(PEt_3)_2$ COMPLEXES



from the effect of spin-orbit coupling in coupling of the $^4T_1(P)$ state to close-lying doublet states.[89]

The charge transfer bands found at higher energy are also split to a considerable extent, again possibly due to a distortion from tetrahedral symmetry which increases with increasing halogen size. The band near 285 nm in the spectra of the three complexes (Table 2.25 and Fig. 2.23) is virtually invariant with change in halogen and hence can be reasonably assigned to a phosphine-metal charge transfer transition. The other charge transfer transition at lower energy varies with change in halogeno-ligand in the manner discussed for the similar band in mononuclear square planar complexes, and thus this band may be analogously assigned to a halogen → metal charge transfer transition.

Section 2.3 Preparation of Four-Coordinate Complexes

Discussion

(a) Complexes of cobalt (II) and nickel (II):-

For chloro and bromo complexes of cobalt (II) and nickel (II) the preparative method used was to add the ligand, in small excess, to an ethanolic solution of the appropriate metal (II) halide. The reaction was carried out at room temperature and under an atmosphere of dry, oxygen-free dinitrogen. For iodo complexes it was necessary to prepare first the metal (II) iodide which was then dissolved in ethanol and treated with the ligand. The complex $CoCl_2(PEt_3)_2$ is rather unstable with respect to oxidation of the ligand to the phosphine oxide[46], and hence the compound was stored under a dinitrogen atmosphere. The complexes $CoCl_2(Et_2PhP)_2$ and $CoI_2(Et_2PhP)_2$ were obtained as oils which failed to crystallise.

(b) Mononuclear complexes of palladium (II):-

Complexes of the type $PdX_2(phosphine)_2$ were prepared by the general method of shaking a concentrated aqueous solution of the appropriate potassium tetrahalogenopalladite (II) salt with the ligand, followed by recrystallisation. The K_2PdX_4 salts were prepared as discussed in Chapter 6 (p.185). While the trans isomer is generally favoured for these palladium (II) phosphine complexes[45] it has been observed[63] that the cis isomers of some chloro complexes of mixed alkyl/aryl phosphine ligands can be isolated in certain cases. Thus Grim and Keiter[64] have prepared the cis isomer of dichlorobis (diethylphenylphosphine) palladium (II) by utilizing the fact that the trans isomer is moderately soluble in light petroleum whereas the cis isomer is insoluble, and this preparative method has been used in the present work to achieve a satisfactory separation of the isomers.

(c) Mononuclear complexes of platinum (II):-

Treatment of an aqueous solution of a potassium tetrahalogenoplatinite (II) salt with either of triethylphosphine or diethylphenylphosphine gave a cream-coloured powdery product which was a mixture of cis and trans isomers. Jensen[137] achieved a reasonable separation of these isomers by extracting the trans isomer with light petroleum and recovering the insoluble cis isomer from the residue. Chatt and Wilkins[30,60] have discussed the equilibrium between the isomers and have detailed a more specific isomerisation procedure; their methods have been used in the present work.

For the iodo complexes only the trans isomer is formed in the reaction of K_2PtI_4 with either phosphine. The cis isomers were obtained by a two-step synthesis[138] involving the preparation

of the sulphato complex, $Pt(phosphine)_2SO_4$, and the reaction of this material with potassium iodide.

Triethylphosphite complexes of platinum (II) were prepared by adding the ligand in excess to aqueous solutions of K_2PtX_4 salts.[139]

(d) Binuclear complexes of palladium (II) and platinum (II):-

Binuclear complexes of form $M_2Cl_4L_2$ (M = Pd(II) or Pd(II); L = PEt_3) were prepared by either reaction of MCl_2L_2 with K_2MCl_4 in ethanol boiling under reflux (M = Pd(II)) or reaction of the metal (II) chloride with MCl_2L_2 as a slurry in a high boiling hydrocarbon solvent (M = Pt(II)). The bromo and iodo complexes for both palladium (II) and platinum (II) were obtained by metathetical reaction of the binuclear chloro complex with lithium bromide or sodium iodide respectively.

(e) Complexes of zinc (II):-

The preparation of zinc (II) complexes of the form $ZnX_2(phosphine)_2$ was achieved by adding the required ligand to a 50% ethanol solution of the appropriate zinc (II) halide. The complexes increase in stability towards ligand dissociation[90] in the order Cl < Br < I and Et_2PhP < PEt_3. In the present work the complex $ZnCl_2(Et_2PhP)_2$ could not be obtained in a satisfactory crystalline form.

(f) Attempted preparation of some rhodium (I) complexes:-

Wilkinson et al.[140] showed that the reaction of rhodium trichloride hydrate with excess triphenylphosphine gave the rhodium (I) complex, $RhCl(Ph_3P)_3$. The conditions are important since if the ligand is not in excess the only reaction product[140]

is the rhodium (III) complex, $RhCl_3(Ph_3P)_3$. Chatt and co-workers[141] attempted to prepare mixed alkyl/aryl phosphine analogues of $RhCl(Ph_3P)_3$ using Wilkinson's method but the only product, regardless of the conditions, was trichlorotris (phosphine) rhodium (III).

It was of interest in the present work to attempt to prepare halogenotris (phosphine) rhodium (I) complexes with PEt_3 or Et_2PhP, as further extensions of the work on four-coordinate complexes. Since it appears certain[140,141] that the formation of $RhCl(Ph_3P)_3$ by reduction with the phosphine ligand is unique to triphenylphosphine it was necessary to try alternative methods of producing the desired compounds. These were as follows.

(i) Bennett and Milner[142,143] have shown that triphenylphosphine will react with the complex $[Ir(COD)Cl]_2$ (COD = cyclooctadiene) to give the iridium (I) analogue of $RhCl(Ph_3P)_3$. In this work the analogous reaction of $[Rh(COD)X]_2$ (X = Cl,Br) with PEt_3 gave products which could not be obtained in crystalline form. The ^1H NMR spectra of these oily products contained the ligand as impurity and hence it was not possible to decide if the expected product was present.

(ii) While the work described in (i) above was in progress a report on the preparation of $RhCl(PEt_3)_3$ and some related compounds appeared in the literature.[144] This method involved reducing rhodium trichloride in benzene/ethanol solution with ethylene, and treating the product so formed with the phosphine ligand. However, numerous attempts to repeat this procedure in the present work were unsuccessful.

Experimental Details

(a) Complexes of nickel (II) and cobalt (II) :-

A representative preparation is as follows. Dibromobis (triethylphosphine)cobalt(II), $CoBr_2(PEt_3)_2$ [145] :-

A solution of cobalt (II) bromide hexahydrate (0.3gm) in ethanol (25ml) was treated with PEt_3 (0.3gm). A light blue crystalline precipitate was immediately formed and this was filtered off, recrystallised from ethanol, and dried in vacuo (0.36gm, 86%). The fine, light blue needles had m.pt. 132-134° c f. lit.[145] 134-136°. Analysis : Calculated for $C_{12}H_{30}Br_2P_2Co$, C = 31.6%; H = 6.59%. Found : C = 31.5%; H = 6.52%.

The following compounds were prepared similarly. Dichlorobis(triethylphosphine)cobalt(II), $CoCl_2(PEt_3)_2$ [46] :-

Dark blue needles, from ethanol (80%). m.pt. 98° c f. lit.[46] 101-102°. Analysis : Calculated for $C_{12}H_{30}Cl_2P_2Co$, C = 39.3%; H = 8.19%. Found : C = 39.2%; H = 8.12%.

Trans - dichlorobis(triethylphosphine)nickel(II), $NiCl_2(PEt_3)_2$ [46] :-

Maroon needles, from ethanol (86%). m.pt. 112° c f. lit.[46] 112-113°. Analysis : Calculated for $C_{12}H_{30}Cl_2P_2Ni$, C = 39.3%; H = 8.19%. Found : C = 39.5%; H = 8.31%.

Trans-dibromobis(triethylphosphine)nickel(II), $NiBr_2(PEt_3)_2$ [46]:-

Maroon needles, from ethanol (83%). m.pt. 103-104° c f.lit.[46] 106-107°. Analysis: Calculated for $C_{12}H_{30}Br_2P_2Ni$, C = 31.6%; H = 6.59%. Found : C = 31.8; H = 6.52%.

Dibromobis(diethylphenylphosphine)cobalt(II), $CoBr_2(Et_2PhP)_2$ [145] :-

Sea-green needles, from ethanol (75%). m.pt. 80-82°

c f. lit.[145] 80-82°. Analysis : Calculated for $C_{20}H_{30}Br_2P_2Co$, C = 43.6%; H = 5.44%. Found : C = 43.9%; H = 5.66%.

Trans-dichlorobis(diethylphenylphosphine)nickel(II), $NiCl_2(Et_2PhP)_2$:-

Maroon needles, from ethanol (77%). m.pt. 113°. Analysis : Calculated for $C_{20}H_{30}Cl_2P_2Ni$, C = 51.9%; H = 6.49%. Found : C = 52.1%; H = 6.54%.

Trans-dibromobis(diethylphenylphosphine)nickel(II), $NiBr_2(Et_2PhP)_2$[48] :-

Maroon crystals, from ethanol (80%). m.pt. 114-115° c f.lit.[48] 114-116°. Analysis : Calculated for $C_{20}H_{30}Br_2P_2Ni$, C = 43.6%; H = 5.44%. Found : C = 43.7%; H = 5.46%.

Diiodobis(triethylphosphine)cobalt(II), $CoI_2(PEt_3)_2$[46] :-

Crude cobalt(II) iodide containing iodine impurity was refluxed in ethanol for several hours and the brown solution so formed was filtered from insoluble material. The addition of triethylphosphine to this solution gave green microcrystals of the required complex (58%). m.pt. 118° c f.lit.[46] 118-120°. Analysis : Calculated for $C_{12}H_{30}I_2P_2Co$, C = 26.2%; H = 5.46%. Found : C = 26.7%; H = 5.63%.

Trans-diiodobis(triethylphosphine)nickel(II), $NiI_2(PEt_3)_2$[46] :-

Nickel(II) iodide was prepared by the method of Brauer.[146] This involved repeated treatment of nickel carbonate with concentrated hydriodic acid and heating the system to dryness. Black crystals of the iodide were obtained after three such treatments. The hydriodic acid was prepared by distilling commercial HI from red phosphorus.

The nickel iodide prepared as above was treated with

PEt_3 to give dark brown needles of the required complex (74%). m.pt. 88-89° c.f.lit.[46] 91-92°. Analysis : Calculated for $C_{12}H_{30}I_2P_2Ni$, C = 26.2%; H = 5.46%. Found : C = 26.4%; H = 5.82%.

Trans-diiodobis(diethylphenylphosphine)nickel(II), $NiI_2(Et_2PhP)_2$:-

Black microcrystals, from ethanol (70%). m.pt. 87-88°. Analysis : Calculated for $C_{20}H_{30}I_2P_2Ni$, C = 37.2%; H = 4.65%. Found : C = 37.2%; H = 4.73%.

(b) Mononuclear palladium (II) complexes :-

A typical preparation is as follows.

Trans-dichlorobis(triethylphosphine)palladium(II), $PdCl_2(PEt_3)_2$ [67] :-

K_2PdCl_4 (0.5gm) dissolved in cold water was treated with PEt_3 (0.5gm). The mixture was shaken for 10 minutes and the yellow product which formed was extracted with chloroform. The extract was dried over anhydrous sodium sulphate and evaporated to dryness to yield yellow crystals, recrystallised from ethanol (0.43gm, 68%). m.pt. 137-138° c.f.lit.[67] 139°. Analysis : Calculated for $C_{12}H_{30}Cl_2Pd$, C = 34.9%; H = 7.26%. Found : C = 34.6%; H = 7.69%.

The following compounds were similarly prepared.

Trans-dibromobis(triethylphosphine)palladium(II), $PdBr_2(PEt_3)_2$ [67] :-

Yellow prisms, from ethanol (81%). m.pt. 134-135°. c.f.lit.[67] 136°. Analysis : Calculated for $C_{12}H_{30}Br_2P_2Pd$, C = 28.7%; H = 5.98%. Found : C = 29.2%; H = 6.03%.

Trans-diiodobis(triethylphosphine)palladium(II), $PtI_2(PEt_3)_2$ [67] :-

Orange prisms, from ethanol (77%). m.pt. 138-139° c f.lit.[67] 139°. Analysis : Calculated for $C_{12}H_{30}I_2P_2Pd$, C = 24.2%; H = 5.03%. Found : C = 24.3%; H = 5.04%.

Trans-dibromobis(diethylphenylphosphine)palladium(II), $PdBr_2(Et_2PhP)_2$ [147] :-

Yellow needles, from ethanol (72%). m.pt. 135° c f.lit.[147] 132-133°. Analysis : Calculated for $C_{20}H_{30}Br_2P_2Pd$, C = 40.1%; H = 5.02%. Found : C= 40.4%; H = 5.21%.

Trans-diiodobis(diethylphenylphosphine)palladium(II), $PdI_2(Et_2PhP)_2$:-

Red-orange prisms, from ethanol (66%). m.pt. 123-124°. Analysis : Calculated for $C_{20}H_{30}I_2P_2Pd$, C = 34.7%; H = 4.34%. Found : C = 34.7%; H = 4.37%.

Trans-dichlorobis(diethylphenylphosphine)palladium(II), $PdCl_2(Et_2PhP)_2$ [64] :-

Yellow needles, from light petroleum (50%). m.pt. 141° c f.lit.[103] 129°. Analysis : Calculated for $C_{20}H_{30}Cl_2P_2Pd$, C = 47.2%; H = 5.89%. Found : C = 47.4%; H = 5.87%.

Cis-dichlorobis(diethylphenylphosphine)palladium(II), $PdCl_2(Et_2PhP)_2$ [64] :-

The cis isomer was obtained as pale lemon microcrystals by recrystallising from ethanol the residue remaining after light petroleum extraction of the trans isomer from the crude mixture. (10%). m.pt. The compound softens at 132° and appears to convert to the trans isomer, since it melts at 141° c f.lit.[64] 139°. Analysis : Calculated for $C_{20}H_{30}Cl_2P_2Pd$, C = 47.2%; H = 5.89%. Found: C = 47.0%; H = 5.93%.

(c) Mononuclear complexes of platinum(II) :-

A typical preparation is as follows.

Dichlorobis(triethylphosphine)platinum(II), $PtCl_2(PEt_3)_2$ [60] :-

trans isomer :-

Crude $PtCl_2(PEt_3)_2$ (0.30gm) was dissolved in benzene (20ml) and PEt_3 (0.002gm) added from a microsyringe. The system was allowed to reach equilibrium (30 minutes) and $Pt_2Cl_4(PEt_3)_2$ (0.006gm) was added. The solution was evaporated to dryness under reduced pressure and the residue dried in vacuo. The dry product was extracted with light petroleum (50-70) to give a pale yellow solution and a small white residue of the cis isomer. The extract was twice recrystallised from ethanol to give pale lemon needles (0.22gm, 73%) m.pt. 139° c.f.lit.[67] 142°. Analysis : Calculated for $C_{12}H_{30}Cl_2P_2Pt$, C = 28.7%; H = 5.98%. Found : C = 29.4%; H = 5.91%.

cis isomer :-

The crude complex (0.30 gm) was suspended in warm light petroleum (50-70, 30ml) and PEt_3 (0.005gm) in light petroleum (1ml) was added. Ten minutes was allowed for equilibration and the solvent was taken off at reduced pressure. The residue was further dried in vacuo and then washed with light petroleum. Recrystallisation from ethanol gave white prisms of the cis isomer (0.22gm, 73%). m.pt. 188-189° c.f.lit.[67] 197°. Analysis : Calculated for $C_{12}H_{30}Cl_2P_2Pt$, C = 28.7%; H = 5.98%. Found : C = 28.8%; H = 5.92%.

The following compounds were prepared using the above procedure :-

Cis-dibromobis(triethylphosphine)platinum(II), cis- $PtBr_2(PEt_3)_2$ [67] :-

White needles, from ethanol (58%). m.pt. 194° c.f.lit.[67] 192°. Analysis : Calculated for $C_{12}H_{30}Br_2P_2Pt$, C = 24.4%; H = 5.08%. Found : C = 24.8%; H : 5.27%.

Trans-dibromobis(triethylphosphine)platinum(II), trans-$PtBr_2(PEt_3)_2$ [67] :-

Yellow needles, from ethanol (70%). m.pt. 136°. c.f.lit.[67] 135°. Analysis : Calculated for $C_{12}H_{30}Br_2P_2Pt$, C = 24.4%; H = 5.08%. Found : C = 24.7%; H = 4.97%.

Trans-diiodobis(triethylphosphine)platinum(II), trans-$PtI_2(PEt_3)_2$ [67] :-

Yellow needles, from ethanol (81%). m.pt. 136° c.f.lit.[67] 136°. Analysis : Calculated for $C_{12}H_{30}I_2P_2Pt$, C = 21.0%; H = 4.38%. Found : C = 21.5%; H = 4.47%.

Cis- dichlorobis(diethylphenylphosphine)platinum(II), cis-$PtCl_2(Et_2PhP)_2$ [59] :-

White prisms, from ethanol (72%). m.pt. 203° c.f.lit.[59] 202-203°. Analysis : Calculated for $C_{20}H_{30}Cl_2P_2Pt$, C = 40.1%; H : 5.02%. Found : C = 39.8%; H = 5.03%.

Cis-dibromobis(diethylphenylphosphine)platinum(II), cis-$PtBr_2(Et_2PhP)_2$:-

White prisms, from ethanol (75%). m.pt. 183°. Analysis : Calculated for $C_{20}H_{30}Br_2P_2Pt$, C = 34.9%; H = 4.37%. Found : C = 35.6%; H = 4.72%.

Trans-diiodobis(diethylphenylphosphine)platinum(II), trans-$PtI_2(Et_2PhP)_2$:-

Yellow needles, from ethanol (80%). m.pt. 139°. Analysis : Calculated for $C_{20}H_{30}I_2P_2Pt$, C = 30.7%; H = 3.84%. Found : C = 30.7%; H = 3.99%.

The complexes trans-$PtCl_2(Et_2PhP)_2$ and trans-$PtBr_2(Et_2PhP)_2$ could not be obtained in a satisfactory crystalline form.

Cis-diiodobis(triethylphosphine)platinum(II), cis-$PtI_2(PEt_3)_2$ [138] :-

(i) Sulphatobis(triethylphosphine)platinum(II), $Pt(PEt_3)_2SO_4$:-

Crude $PtCl_2(PEt_3)_2$ (0.2gm) was dissolved in hot ethanol and shaken with silver sulphate (0.8gm) until no further precipitate was obtained on testing the solution with silver nitrate solution. Yellow crystals of $Pt(PEt_3)_2SO_4$ were obtained after filtration and evaporation.

(ii) Cis-diiodobis(triethylphosphine)platinum(II), cis-$PtI_2(PEt_3)_2$:-

An aqueous solution of $Pt(PEt_3)_2SO_4$ prepared as in (i) above was treated with an aqeous solution of potassium iodide. A buff-coloured solid precipitated and this was filtered off and recrystallised from ethanol to give yellow prisms (0.21gm, 77%). The compound isomerised to the trans form on heating above 110° and melted at 135°. Analysis : Calculated for $C_{12}H_{30}I_2P_2Pt$, C = 21.0%; H = 4.38%. Found : C = 21.5%; H = 4.38%.

Cis-diiodobis(diethylphenylphosphine)platinum(II), cis-$PtI_2(Et_2PhP)_2$:-

A similar preparation to that given above for the triethylphosphine analogue gave yellow microcrystals, from ethanol (61%). m.pt. converts to trans, 139°. Analysis : Calculated for $C_{20}H_{30}I_2P_2Pt$, C = 30.7%; H = 3.84%. Found : C = 30.6%; H = 3.81%.

Triethylphosphite complexes of platinum(II) were prepared

as colourless oils which failed to crystallise (chloro and bromo complexes), or as yellow oily crystals (iodo complex) as below.

Cis-diiodobis(triethylphosphite)platinum(II), cis-$PtI_2\{P(OEt)_3\}_2$ [139] :-

Aqueous K_2PtI_4 solution was treated with excess $P(OEt)_3$. Yellow crystals of the required complex were immediately formed and these were filtered off and recrystallised from ethanol (58%). m.pt. 82° c.f.lit.[139] 86°. Analysis : Calculated for $C_{12}H_{30}I_2O_6P_2Pt$, C = 18.4%; H = 3.84%. Found : C = 19.1%; H = 3.97%.

All three complexes, cis-$PtX_2\{P(OEt)_3\}_2$ (X = Cl,Br,I), gave satisfactory ^1H NMR spectra (see p. 49).

(d) Binuclear complexes of palladium(II) and platinum(II):-

(i) Palladium(II) Di-μ-chloro-dichlorobis (triethylphosphine)dipalladium(II), $Pd_2Cl_4(PEt_3)_2$ [80] :-

$PdCl_2(PEt_3)_2$ (0.7gm) in hot ethanol (70ml) was treated with K_2PdCl_4 (0.5gm) in warm water (10ml) diluted with ethanol (20ml). The mixture was boiled under reflux for 2 hours and then filtered. The orange solution was cooled in ice and the solid so formed was recrystallised from ethanol (0.72gm, 72%). m.pt. 232° c.f.lit.[80] 230°. Analysis : Calculated for $C_{12}H_{30}Cl_4P_2Pd_2$, C = 24.4%, H = 5.08%. Found C = 25.1%, H = 5.37%.

Di-μ-bromo-dibromobis(triethylphosphine)dipalladium(II), $Pd_2Br_4(PEt_3)_2$:-

The chloro complex (0.25mg) and lithium bromide (2gm) were placed in acetone (40ml) and the solution boiled under reflux for 2 hours. The solvent was evaporated under reduced pressure and the product washed with hot water. Recrystallisation from ethanol gave orange-red crystals (0.20gm, 61%) m.pt. 214° c.f.lit.[85] 212-213°.

Analysis : Calculated for $C_{12}H_{30}Br_4P_2Pd_2$; C = 18.8%; H = 3.91%. Found : C = 18.3%; H = 4.60%.

Di-μ-iodo-diiodobis(triethylphosphine)dipalladium(II), $Pd_2I_4(PEt_3)_2$ [85] :-

A similar metathetical preparation to that given above for the bromo complex, but using sodium iodide in place of lithium bromide, gave red crystals of the required complex after recrystallisation from ethanol (69%). m.pt. 193° c.f.lit.[85] 191-192°. Analysis : Calculated for $C_{12}H_{30}I_4P_2Pd_2$, C = 15.1%; H = 3.14%. Found : C = 15.6%; H = 3.26%.

(II) Platinum (II) :- Di-μ-chloro-dichlorobis (triethylphosphine)diplatinum(II), $Pt_2Cl_4(PEt_3)_2$ [82] :-

$PtCl_2(PEt_3)_2$ (0.6gm) and $PtCl_2$ (0.35gm)[148] were finely ground in a mortar. This intimate mixture was added to xylene (25ml) and boiled under reflux for 2 hours. The solution was cooled and washed well with light petroleum. The product was extracted with dichloromethane (20ml) and recrystallised from chloroform to give orange crystals (0.62gm, 65%). m.pt. 223-224° c.f.lit.[81] 223-224°. Analysis : Calculated for $C_{12}H_{30}Cl_4P_2Pt_2$, C = 18.8%; H = 3.91%. Found : C = 18.9%; H = 3.82%.

The bromo and iodo complexes were prepared by analogous metathetical reactions to those given above for the binuclear palladium complexes.

Di-μ-bromo-dibromobis(triethylphosphine)diplatinum(II), $Pt_2Br_4(PEt_3)_2$ [85] :-

Orange-red crystals, from chloroform (71%). m.pt. 202° c.f.lit.[85] 202°. Analysis : Calculated for $C_{12}H_{30}Br_4P_2Pt_2$, C = 15.2%; H = 3.17%. Found : C = 15.7%; H = 3.29%.

Di-μ-iodo-diiodobis(triethylphosphine)diplatinum(II), $Pt_2I_4(PEt_3)_2$ [85] :-

Red crystals, from chloroform (81%). m.pt. 210° c.f.lit.[85] 209-210°. Analysis : Calculated for $C_{12}H_{30}I_4P_2Pt_2$, C = 12.7%; H = 2.65%. Found : C = 12.9%; H = 2.58%.

(e) Complexes of zinc(II) :- A typical preparation is as follows

Dichlorobis(triethylphosphine)zinc(II), $ZnCl_2(PEt_3)_2$ [91] :-

White microcrystals, from ethanol (51%). m.pt 96-97° c.f.lit.[91] 97-98°.. Analysis : Calculated for $C_{12}H_{30}Cl_2P_2Zn$, C = 38.7%; H = 8.06%. Found : C = 38.3%; H = 7.98%.

Dibromobis(triethylphosphine)zinc(II), $ZnBr_2(PEt_3)_2$ [91] :-

White microcrystals, from ethanol (70%). m.pt. 140-142°. c.f.lit.[91] 130°. Analysis : Calculated for $C_{12}H_{30}Br_2P_2Zn$, C = 31.2%; H = 6.50%. Found : C = 31.0%; H = 6.52%.

Diiodobis(triethylphosphine)zinc(II), $ZnI_2(PEt_3)_2$:-

White prisms, from ethanol (73%). m.pt. 162-163°. Analysis : Calculated for $C_{12}H_{30}I_2P_2Zn$, C = 25.9%; H = 5.41%. Found : C = 25.9%; H = 5.64%.

Dibromobis(diethylphenylphosphine)zinc(II), $ZnBr_2(Et_2PhP)_2$:-

White microcrystals, from ethanol (74%). m.pt. 66-68°. Analysis : Calculated for $C_{20}H_{30}Br_2P_2Zn$, C = 43.1%; H = 5.39%. Found : C = 42.7%; H = 5.12%.

Diiodobis(diethylphenylphosphine)zinc(II), $ZnI_2(Et_2PhP)_2$:-

White microcrystals, from ethanol (79%). m.pt. 94-95°. Analysis : Calculated for $C_{20}H_{30}I_2P_2Zn$, C = 36.9%; H = 4.61%. Found : C = 36.5%; H = 4.92%.

(f) Attempted preparation of rhodium(I) complexes :-

Method (i) [142,143] :-

$[Rh(COD)Cl]_2$, prepared by the method of Chatt and Venanzi,[149] was dissolved in light petroleum (50-70) and boiled under reflux with excess of triethylphosphine for 2 hours. After evaporation of the solvent at reduced pressure a product was obtained as a red-brown oil which could not be crystallised. Repeated attempts using this method were all unsuccessful, and the bromo and iodo COD complexes both gave oils as well, on treatment with PEt_3.

Method (ii) [144] :-

$RhCl_3.3H_2O$ (1gm) was dissolved in ethanol/benzene solution (100ml) and ethylene bubbled through the refluxing solution for 24 hours. After cooling the solution was treated with excess of PEt_3 and dinitrogen was then vigorously bubbled through the solution for 2 days. The dark red solution was filtered and the solvent evaporated under reduced pressure. The red-brown oily product could not be crystallised and the ^1H NMR spectrum of the product was not definitive because of obscuring free ligand peaks.

The oily product obtained above was treated with lithium bromide in acetone and the solution boiled under reflux. A brown crystalline material was obtained after the work-up. However the analytical figures of C = 27.6%; H = 6.49% are not consistent with $RhBr(PEt_3)_3$ which required C = 40.1%; H = 8.38%, $[RhBr(PEt_3)_2]_n$ which required C = 34.4%; H = 7.16%, or $RhBr_3(PEt_3)_3$ which requires C = 30.9%; H = 6.46%. This rhodium(I) system was not further investigated.

CHAPTER 3

ASPECTS OF THE PHOSPHINE CHEMISTRY OF RHENIUM AND TECHNETIUM

The work discussed in this Chapter is divided into the following three sections ;

3.1 Spectroscopic studies of rhenium (V) phosphine complexes containing oxo or nitrido ligands. These complexes have the stoichiometry $ReOX_3L_2$ or $ReNX_2L_3$ where X = Cl,Br or I, and L = PEt_3 or Et_2PhP. The complexes have been studied by ^1H and ^{13}C NMR, far infra-red and electronic absorption spectroscopy.

3.2 Preparative, structural and spectroscopic studies of rhenium nitrosyl complexes of general formula $ReX_3(NO)L_2$ (X = Cl,Br or I; L = Et_2PhP). The spectroscopic techniques used here were far infra-red, ^1H NMR, and electronic absorption spectroscopy.

3.3 Preparative aspects of the phosphine chemistry of technetium.

SECTION 3.1. RHENIUM (V) OXO AND NITRIDO COMPLEXES

3.1.1 Introduction

This introduction is restricted to an outline of previous results which are related to the work carried out in this thesis.

(a) Oxo complexes of rhenium (V) :-

The triphenylphosphine complex of rhenium (V), $ReOCl_3(Ph_3P)_2$, is a useful starting material for the preparation of other rhenium complexes. For example ligand substitution

reactions with either trialkyl or mixed alkyl/aryl phosphines in benzene solution result in a replacement[150] of Ph_3P by the other phosphines. This is a convenient route to the oxo complexes studied in the present work. The compounds may also be obtained directly by reaction of the required phosphine ligand with perrhenic acid in ethanol containing concentrated hydrochloric acid.[151-154] Two isomeric forms can be isolated for the chloro complexes.[152,153] The green form of $ReOCl_3(Et_2PhP)_2$ has been shown by dipole moment measurements to be the trans isomer[153] and this was confirmed by a single crystal X-ray structure determination[155] of the Et_2PhP complex. The blue form has been assigned to a cis arrangement on the basis of a dipole moment[153] of 10.8 D, without distinguishing between the two possibilities (see Figure 3.1). The preparation with perrhenic acid as starting material also leads to a third product, which is violet in colour.[153] This has been shown[150] to be a solid solution containing 15% $ReCl_4L_2$ and 85% trans-$ReOCl_3L_2$. The bromo[150] and iodo[153] analogous with Et_2PhP as ligand have been prepared using the perrhenic acid reduction method with hydrobromic or hydriodic acid respectively. Dipole moment measurements were considered to indicate a cis arrangement of phosphine ligands.[150,153]

The complexes are diamagnetic in the solid state and in solution.[154] This is unexpected for a d^2 configuration in a regular octahedral environment. However, the influence of the short rhenium-oxygen bond reduces the octahedral symmetry to C_{2v} in the trans complexes (or C_s in the cis case), in which a low-lying a_1 orbital is available for accommodating the two electrons.[156] The Re-O bond length is very short (160pm)[155] and suggests a bond order of three. This is achieved by the formation of two Re-O π bonds between oxygen lone pairs contained

in p_x and p_y orbitals and the vacant $d_{yz,xz}$ metal orbitals, in addition to the normal σ bond. π bonding between the metal and the other ligands[157] involves all other rhenium valence orbitals except the d_{xy} (a_1) (Fig. 3.4) orbital which can then accommodate the two electrons of the d^2 configuration, giving a spin paired complex.

The sharp intense band in the 958-985 cm^{-1} range of the infra-red spectra of the oxo complexes has been assigned[151-154,156] to the rhenium-oxygen asymmetric stretching vibration. This high frequency is further evidence of the multiple nature of the Re-O bond. In addition the oxo ligand of these complexes cannot be protonated whereas protonation is possible for the trans-dioxo complexes of formula $[ReO_2(en)_2]^+$ and $[ReO_2(py)_4]^+$ where the Re-O bond order is considered to be lower.[154]

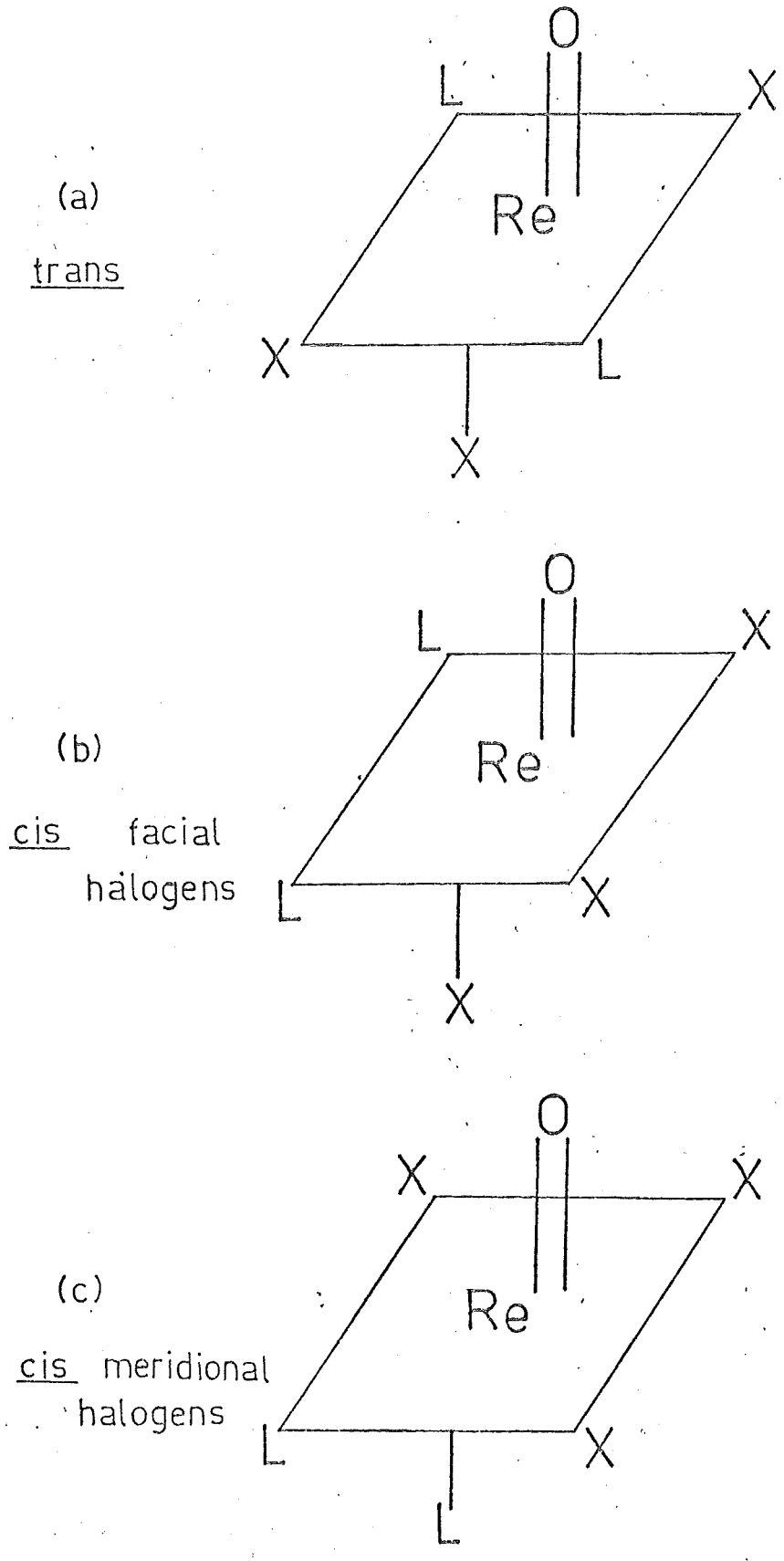
Apart from studies of the metal-oxygen stretching frequencies little other spectroscopic work has been reported on these oxo complexes of rhenium (V). The ^1H NMR spectrum[150] of trans-$ReOCl_3(Et_2PhP)_2$ has been reported and the electronic spectrum of the same complex has also been mentioned.[150]

(b) Rhenium (V) nitrido complexes :-

The reduction of perrhenic acid with hydrazine hydrochloride in the presence of Ph_3P and water was originally claimed to give $ReCl_2(Ph_3P)_2$.[153,158,159] However later studies[160] showed that the compound was a nitrido (N^{3-}) complex of rhenium (V), $ReNCl_2(Ph_3P)_2$. Phosphines such as Et_2PhP give rise to six-coordinate $ReNCl_2L_3$ complexes.[161] The single crystal X-ray structures of $ReNCl_2(Ph_3P)_2$[162] and $ReNCl_2(Et_2PhP)_3$[163] have been determined and in both cases the Re-N bond length is short

FIGURE 3·1

POSSIBLE ISOMERS OF $ReOX_3L_2$ COMPLEXES



(160pm and 178pm respectively). This, together with the assignment of a sharp band near 1050cm^{-1} in the infra-red spectra to ν(Re-N), establishes the triple bond character of the rhenium-nitrogen linkage. The six-coordinate Et_2PhP complex deviates significantly from regular octahedral symmetry.[163] The diamagnetism can be explained along similar lines to those discussed for the oxo complexes. Only one isomeric form has been found for the six coordinate nitrido complexes. This has one of the chlorides *trans* to the nitrido ligand and the rhenium-chlorine bond length (256pm) is significantly longer than that of the other rhenium-chlorine bond (245pm) *trans* to a phosphine ligand.[163] The nitrido ligand thus exerts a considerable *trans* influence (see later discussion) on the Re-Cl bond *trans* to it.

The low frequency infra-red spectra of $ReNCl_2(Et_2PhP)_3$ and $ReNBr_2(Et_2PhP)_3$ have been briefly discussed[164] by Chatt et al. The ^{1}H NMR spectrum of $ReNCl_2(Et_2PhP)_3$ has also been reported.[161]

3.1.2 Results and Discussion

(a) Stereochemistry of the oxo complexes :-

There are three possible isomers of the complex of general formula $ReOX_3L_2$ and these are represented in Figure 3.1. It is necessary to establish first the stereochemistry of the complexes prepared and studied in this work before analysing the spectra obtained.

The green and blue isomers of the chloro complexes for both PEt_3 and Et_2PhP phosphine ligands have been prepared in this work. The green complexes have a *trans* arrangement of phosphine ligands as shown by ^{1}H NMR where the phenomenon of

virtual coupling between trans phosphorus nuclei (Chapter 2) gives rise to a quintet methyl resonance with intensity ratio 1:4:6:4:1. The way in which this intensity ratio arises has been discussed in Chapter 2 for square planar complexes with a trans arrangement of phosphines. Thus the green $ReOCl_3L_2$ complexes are assigned structure 3.1(a). As noted in the introduction to this section this assignment is confirmed by the single crystal X-ray structure determination[155] for the green form of $ReOCl_3(Et_2PhP)_2$.

The blue chloro isomers have ^1H NMR spectra where the methyl resonance multiplet is a quintet with intensity ratio 1:2:2:2:1. This is expected on the basis of the lack of virtual coupling for cis phosphorus nuclei (Chapter 2). The way in which the observed intensity ratio arises has been discussed in Chapter 2 for square planar complexes with cis arrangement of phosphine ligands. Thus the blue $ReOCl_3L_2$ complexes may be considered to have a cis arrangement of phosphines. Further, since only one environment for the phosphine ligands is apparent from the ^1H NMR spectra of these complexes, this suggests that the complexes have structure 3.1(b). The low frequency infra-red data can also be interpreted in terms of this structure, where the stretching vibration of the rhenium-chlorine bond trans to the oxo ligand is clearly visible (see later discussion).

In the case of the bromo complexes studied here, irrespective of the method of preparation, i.e. reduction of the perrhenate ion with HBr in the presence of the phosphine or metathetical reaction of either the cis or the trans chloro complex with lithium bromide, the product was consistent with a trans arrangement of phosphine ligands as shown by the form

of the methyl multiplet in the ^{1}H NMR spectrum. The 1:4:6:4:1 intensity ratio of this quintet multiplet can be rationalised on the basis of virtual coupling between trans phosphorus nuclei as discussed previously in Chapter 2, and for trans-$ReOCl_3L_2$ complexes above.

The situation is not as clear cut for the iodo complexes. The complexes, prepared by either of the two methods noted above for the bromo analogues, give ^{1}H NMR spectra which show the presence of two different phosphine ligand environments. At first sight this appears to favour structure 3.1(c) for these complexes. However, as shown by the structure determined[155] for trans-$ReOCl_3(Et_2PhP)_2$ this complex is somewhat distorted from regular octahedral symmetry and this distortion may be expected to be more severe in the iodo complexes, since non-bonded interactions between the bulky iodo ligands and the phosphine ligands are likely to be greater than in the analogous chloro and bromo complexes. Thus it seems possible that the iodo complexes could have either structure 3.1(a) or 3.1(b) and still have two different phosphine ligand environments for steric reasons. Therefore ^{1}H NMR studies are not definitive in this case.

Phosphine complexes of other metals also containing three halogens, in which the halogens have the facial arrangement, as in Fig. 3.1(b), are not common except for chloro complexes. For example, in compounds of the type $MX_3(PR_3)_3$ (M = Re,Ru,Os, Rh,Ir), facial and meridional isomers are known for X = Cl[165,166], but fac-$RhBr_3(PEt_3)_3$ is the only known non-chloro complex with a facial arrangement of halogeno-ligands.[166]

Hence the weight of evidence is that structures 3.1(a) and 3.1(b) are adopted by the trans- and cis- oxotrichlorobis

TABLE 3.1

Far Infra-Red Spectra of Rhenium (V) Oxo Complexes (cm^{-1})

ASSIGNMENT	cis-$ReOCl_3(PEt_3)_2$	cis-$ReOCl_3(Et_2PhP)_2$	trans-$ReOCl_3(PEt_3)_2$	trans-$ReOCl_3(Et_2PhP)_2$	trans-$ReOBr_3(PEt_3)_2$	trans-$ReOBr_3(Et_2PhP)_2$	$ReOI_3(PEt_3)_2$	$ReOI_3(Et_2PhP)_2$
ν(Re-X) in plane	320s	322s	309s	326ms	215m	210s	165m,sh	176s
	295s	295s		312s	188m	202s	153s,br	155m
							145s	143m
ν(Re-X) trans to O	220m,br	225ms	222m,br	233m 213w	156s	165ms	135sh,m	133m
ν(Re-P)	266s 247m	276s	265s	260ms	271s	277wm	287ms	276m
	380w,br		380wm	383w,br	371w,br	390w,br	363m	358ms
	171m	156m	338w	295wm	340w,br	310w	305m	323m
Others	156m	111w,br	190wm,br	186wm	311wm	145wm	125sh,w	293m
	81w	85w	144m	145m,br	135sh,w	98w	90m	86w
	52w	43wm	57w		113w			52w

(phosphine) complexes respectively. The bromo compounds studied here appear to have the trans configuration, 3.1(a), while the situation for the iodo complexes is not clear, but structure 3.1(a) would appear the most probable.

(b) Spectroscopic studies on Rhenium (V) complexes :-

The far infra-red, ^{1}H and ^{13}C NMR, and electronic absorption spectra have been obtained for the compounds and the results are listed in Tables 3.1 - 3.7, while some representative spectra are portrayed in Figs. 3.2 and 3.3.

(i) Far infra-red spectroscopy

(a) Assignments for oxo complexes :-

The principal vibrational frequencies have been assigned for the oxo complexes by comparisons between similar complexes differing only in halogeno ligands, or differing only in phosphines. Thus the partial assignments of Table 3.1 have been made.

The most notable feature is the very low value of the stretching frequency of the rhenium-halogen bond trans to the oxo ligand. This may be rationalised on the basis of the high trans influence of the strongly bond oxo ligand. As discussed before the rhenium-oxygen bound can be considered to comprise one σ and two π components, each of which involves lone pairs on the oxo ligand overlapping with suitable vacant metal orbitals. The effect of this will be to partially neutralize the high positive charge on rhenium. Thus the overall electrostatic effect of the metal ion will be lessened and hence the metal-ligand stretching vibrational frequencies may be expected to be lower than would be expected for rhenium in the pentavalent oxidation state. Further this effect will be most marked for the bond trans to the rhenium-oxygen bond since both the d_{xz}

and d_{yz} orbitals (see earlier discussion) are involved in π-bonding with the oxo group, and are thus not available for π-bonding with the other ligands. This argument is supported by the single crystal X-ray structure[155] of trans-$ReOCl_3(Et_2PhP)_2$ where the Re-Cl bond trans to the oxo ligand is longer (247pm) than the Re-Cl bonds trans to each other (242pm). This suggests that the stretching force constants will be different for the two types of rhenium-chlorine bond present in the complex, and hence that the stretching frequency of the longer bond will be lower. However, some caution must be exercised because a contribution from coupling of vibrational modes in these complexes of lowered symmetry is likely to occur. The nitrido complexes, to be considered shortly, have an analogous structure, with one halogen trans to the nitrido ligand, and Chatt et al.[164] have commented similarly in assigning an absorption at 217 cm^{-1} to the Re-Cl stretching vibration trans to the nitrido ligand in $ReNCl_2(Et_2PhP)_3$.

The assignment of the rhenium-phosphorus stretching vibrations in these spectra has been made with some confidence, based on quantitative results from the isotopic substitution studies discussed in Chapter 2. All spectra show a strong band in the 275 $\pm$ 10cm^{-1} region (Table 3.1). For bromo and iodo complexes there are no other strong absorptions above 230cm^{-1} in energy and the rhenium-halogen vibrations for bromo and iodo complexes occur below 230cm^{-1}. Thus it seems reasonable to assign the strong band near 275 cm^{-1} in these complexes to ν(Re-P). For the chloro complexes the band near 275 cm^{-1} may also be assigned to ν(Re-P), since the other strong absorptions in this general region can be assigned to ν(Re-Cl) by comparison with bromo and iodo complexes.

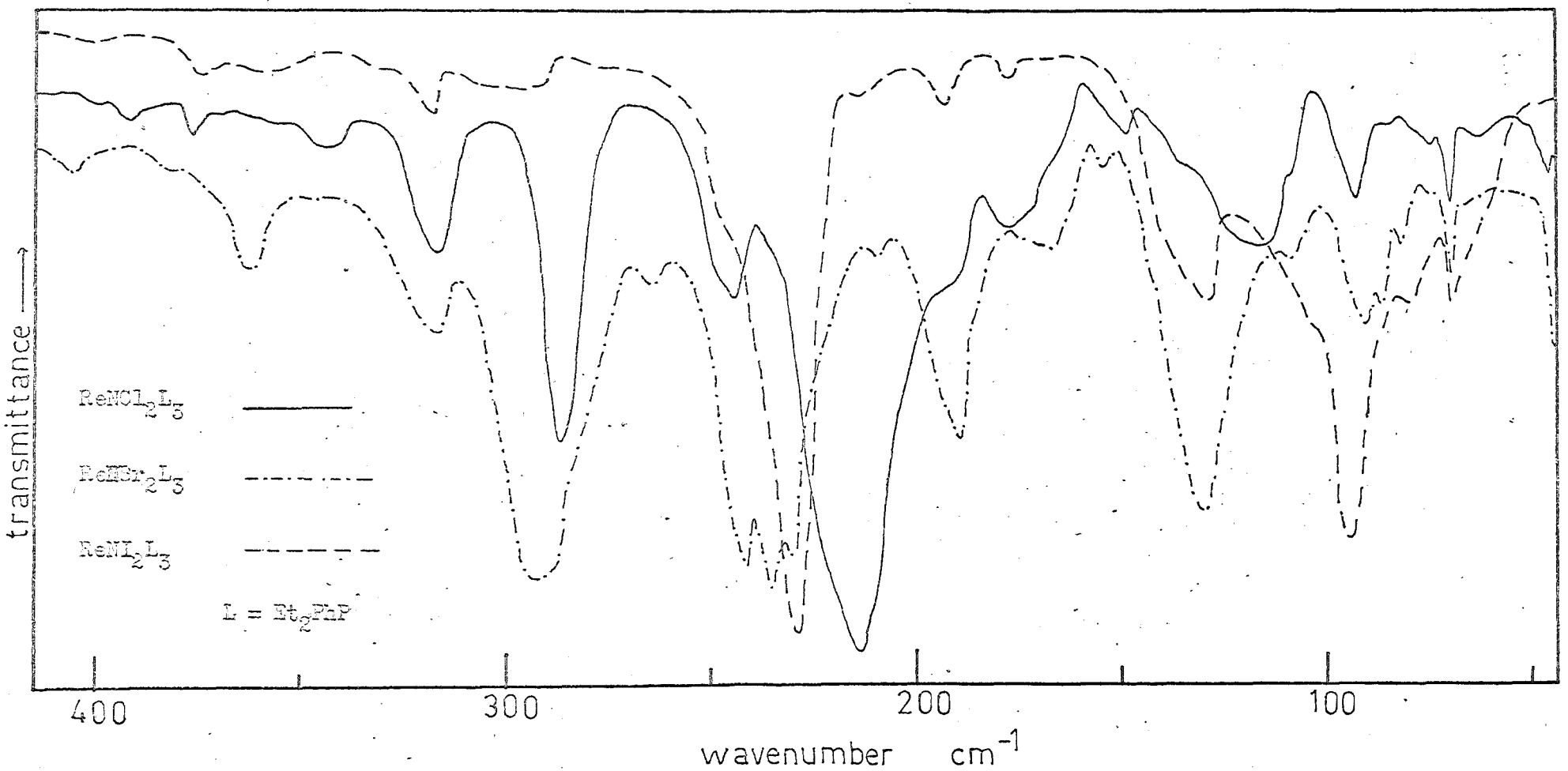
TABLE 3.2

Far Infra-Red Spectra of $ReNX_2(Et_2PhP)_3$ Complexes (X = Cl,Br,I) (cm^{-1})

ASSIGNMENT	$ReNCl_2(Et_2PhP)_3$	$ReNBr_2(Et_2PhP)_3$	$ReNI_2(Et_2PhP)_3$
ν(Re-X) trans to P	282s	190ms	133m
ν(Re-X) trans to N	214s	136ms	94ms
ν(Re-P)	248m,br	240s,vbr	241s
Others	364w,br	361m	370w
	312m	323m	323m
	173w,br	298s,br	295w
	138w,br	95w	168w,br
	98w	45ms	45w
	45w		

FIGURE 3·2

FAR INFRA-RED SPECTRA OF RHENIUM(V) NITRIDO COMPLEXES



(b) Assignments for nitrido complexes :-

Chatt et al.[164] have assigned the rhenium-chlorine stretching frequencies in $ReNCl_2(Et_2PhP)_3$ to two bands separated by c a. 70 cm^{-1}. Thus the strong absorption at 285 cm^{-1} was assigned to ν(Re-Cl) *trans* to phosphorus, and the strong band at 217 cm^{-1} to ν(Re-Cl) *trans* to the nitrido ligand.

The spectrum obtained in this work for $ReNCl_2(Et_2PhP)_3$ is in agreement with that of Chatt and co-workers[164] and the ν(Re-Cl) assignments are listed in Table 3.2. A medium intensity band centred at 248 cm^{-1} is assigned to the rhenium-phosphorus stretching vibration.

The spectrum of the complex $ReNBr_2(Et_2PhP)_3$ has absorptions in similar positions to those listed (but not assigned) by Chatt et al.[164] The band at 190 cm^{-1}, which is of medium-strong intensity, is assigned in the present work to the Re-Br *trans*-to-phosphorus stretching vibration. A further medium-strong band at 136 cm^{-1} is assigned to the Re-Br *trans*-to-nitrido stretching vibration. These assignments have been rationalised by the absence of the bands in question for the chloro analogue. For the bromo complex the rhenium-phosphorus stretching vibration is assigned to the very broad and strong band centred at 240 cm^{-1}. This is similar to the assignment made for the chloro complex.

For $ReNI_2(Et_2PhP)_3$ the assignments are readily made by comparison with the chloro and bromo spectra, and in terms of the expected positions of the relevant absorptions. Thus a medium intensity band at 133 cm^{-1} and a medium-strong band at 94 cm^{-1} have been assigned to ν(Re-I) *trans* to phosphorus and ν(Re-I) *trans* to nitrido respectively. The very strong band at 241 cm^{-1} is assigned to ν(Re-P). This is similar to the

assignments made for this vibration in the chloro and bromo spectra.

(c) Trends in skeletal stretching frequencies for oxo and nitrido complexes :-

Comparisons of the data in Tables 3.1 and 3.2 show several features of interest in these spectra. The first of these is that ν(Re-X) is found at lower energy when trans to the nitrido ligand in $ReNX_2L_3$ complexes than when trans to the oxo ligand in $ReOX_3L_2$ complexes. A similar comparison can be made for the ν(Re-X) frequencies of rhenium-halogen bonds in the equatorial planes of the complexes. Thus ν(Re-Cl) trans to phosphorus in $ReNCl_2(Et_2PhP)_3$ is found at lower energy than the analogous stretching frequency in cis-$ReOCl_3(Et_2PhP)_2$. As discussed previously the high bond order of the Re-O and Re-N bonds will partially neutralize the high positive charge on rhenium in these complexes, and the electrostatic effect of the metal ion will thus be lower. It appears from these results that the nitrido ligand has a greater trans influence than the oxo ligand, which would be expected on the basis of the higher negative charge on the nitrido ligand (N^{3-}) as compared with the oxo ligand (O^{2-}).

The frequencies of rhenium-phosphorus stretching vibrations in the nitrido complexes are also considerably lower than those found for the oxo complexes. This effect may be partially due to the stronger bonding of the nitrido ligand and the reduced electrostatic effect of the metal ion, but the difference in frequency of about 30 cm^{-1} is large and it is possible that coupling of vibrational modes is of importance here.

TABLE 3.3

^{1}H NMR Spectra : Rhenium (V) Oxo Complexes[(a)]

Compound	methyl	methylene	phenyl	ortho
cis-$ReOCl_3(Et_2PhP)_2$	-1.07	-2.33	-7.37	-7.37
trans-$ReOCl_3(Et_2PhP)_2$	-1.25	-2.25	-7.40	-7.59
trans-$ReOBr_3(Et_2PhP)_2$	-1.27	-2.78	-7.43	-7.73
$ReOI_3(Et_2PhP)_2$	-1.00	-1.88 -2.82	-7.28	-7.52
cis-$ReOCl_3(PEt_3)_2$	-1.22	-2.27		
trans-$ReOCl_3(PEt_3)_2$	-1.27	-2.20		
trans-$ReOBr_3(PEt_3)_2$	-1.29	-2.43		
$ReOI_3(PEt_3)_2$	-1.20	-1.75 -2.47		

(a) resonances as ppm downfield from TMS

TABLE 3.4

^{1}H NMR Spectra : Rhenium (V) Nitrido Complexes [(a)]

Compound	methyl	methylene	phenyl	ortho
$ReNCl_2(Et_2PhP)_3$	-1.28	-2.40 -2.90	-7.35	-7.49
$ReNBr_2(Et_2PhP)_3$	-1.23	-2.52 -3.08	-7.74	-8.65
$ReNI_2(Et_2PhP)_3$	-1.13 -1.80	-2.65 -3.37	-7.35	-7.58

(a) resonances as ppm downfield from TMS

(ii) Nuclear magnetic resonance spectra :-

(a) ^{1}H NMR spectra of oxo complexes

Assignment of spectra :-

The assignments made for the ^{1}H NMR spectra of the oxo complexes are listed in Table 3.3. The resonance multiplet for the methyl protons is well resolved in these spectra; however the methylene multiplet is broad and coupling interactions are not well defined.

The form of the methyl multiplets for cis and trans chloro complexes has been discussed previously in this section when considering the stereochemistry of the complexes. The quintet multiplets observed have intensity ratios of 1:2:2:2:1 (cis) and 1:4:6:4:1 (trans), these ratios arising from the absence or presence respectively of the virtual coupling of trans phosphorus nuclei, as discussed in some detail in Chapter 2. The value of the coupling constant $^{2}J(^{31}P\text{-}^{1}H)$ for both cis and trans complexes with Et_2PhP or PEt_3 is 15 Hz .

The methyl region of $ReOBr_3L_2$ complexes has a similar appearance to the trans chloro multiplets and the intensity ratio for the observed quintet is very close to 1:4:6:4:1, $^{2}J(^{31}P\text{-}^{1}H)$ = 15 Hz . There is evidence of a further small second order coupling interaction which causes a slight splitting of the quintet lines. The value of J is no more than 1 Hz for this coupling and in view of the possible non-bonded interactions between the bromo and phosphine ligands in these complexes of low symmetry it seems reasonable to ascribe this effect to a restriction of free rotation about the carbon-carbon bonds.

The spectra of the iodo complexes are consistent with the presence of different environments for the two phosphine

ligands. Thus two resonances are observed for the methylene region and the complex methyl multiplet suggests the overlap of two quintets. The inequivalence of the phosphine ligands could, as noted before, be a result of the complexes having structure 3.1(c) (see Figure 3.1), or the low symmetry and steric effects of the bulky iodo ligands could lead to different phosphine environments. It is of some interest that the dissimilarity of the phosphine environments, as measured by the relative difference in chemical shifts of the two methylene resonances, is most marked for the Et_2PhP complex. The steric requirements of this ligand will presumably be greater than for PEt_3 and hence this may favour the explanation based on the distortions arising from bulky groups.

Trends in the spectra

The phenyl proton resonances for Et_2PhP complexes are of interest. The chloro complex gives a sharp single resonance containing virtually no structure whereasfor the bromo and iodo complexes the ortho protons resonate some 0.30 ppm downfield from the main phenyl resonance. It is felt that the situation for the bromo and iodo complexes is normal, by comparison with analogous results for square planar (Chapter 2) and ruthenium (II) (Chapter 4) complexes with Et_2PhP as ligand. For the chloro complex studied here it may be that the ortho protons move upfield under the influence of non-bonded interactions with the halogens and so coalesce with the main phenyl proton resonance. However why the bromo and iodo complexes do not display a similar effect if this is so, is not clear.

As can be seen in Table 3.3 the methylene multiplet resonance occurs further downfield for the cis chloro complexes

as compared with the trans analogues. The situation is similar to that found for the platinum (and one palladium) complexes discussed in Chapter 2. The conclusions of Chatt and Wilkins[30,31] with regard to the stronger platinum-phosphorus bonds found for cis, as compared with trans, isomers of $PtCl_2(PEt_3)_2$ (p. 28) may thus be extendable to the rhenium complexes, and the deshielding difference might therefore be accounted for by considering that the total bond strength of the rhenium-phosphorus bond when trans to the chloro ligand will be greater than the total bond strength of the analogous bond when trans to the other phosphine ligand. If this is so then the formation of a stronger bond in cis complexes will draw marginally more charge from the organic groups of the tertiary phosphine ligands, thus giving rise to a greater deshielding in the NMR spectrum.

When the halogen is changed from chlorine to bromine there is an increased deshielding of the methylene multiplet resonance. The change in position of the methyl multiplet is negligibly small. These effects have been discussed previously for the palladium and platinum complexes in Chapter 2 and the same arguments may be applied here. The deshielding of the methylene multiplet with change in halogen in the trans complexes could be a result of increased $M_{d\pi} \longrightarrow X_{d\pi}$ interaction between rhenium and bromine, as compared with rhenium and chlorine, with consequent charge draw-off from the phosphine ligand to compensate for the metal charge removed by $d\pi - d\pi$ overlap. In the d^2 rhenium (V) oxo complexes the two electrons are spin-paired in the d_{xy} (a_1) orbital, and are available for π-bonding in the equatorial plane of the complexes.

The deshielding changes might also be explained as arising from metal-ligand bond anisotropy (Chapter 2, p. 46) or from the induced magnetic anisotropy of the metal ion itself (this has also been discussed previously, p. 46). For the latter effect one might expect a correlation between the energy of the ligand field transitions in the electronic spectra and the degree of NMR deshielding. However, this correlation is rather inexact for these rhenium complexes. This may not necessarily negate the explanation in terms of a second-order paramagnetic effect on the NMR resonances, since it is not clear just how the electronic spectral bands will be modified by the lowered symmetry of the complexes, and non-bonded interactions between the ligands. Further discussion is delayed until Chapter 5 where comparisons are made between the various systems studied in this thesis.

(b) ^{1}H NMR spectra of nitrido complexes :-

The ^{1}H NMR spectra of the nitrido complexes indicate, as expected, two phosphine ligand environments in the ratio 2:1. The methyl multiplet is made up of contributions from each environment overlapping to produce a complex resonance (Table 3.4). The methylene resonance for the two phosphines trans to each other is found upfield from the smaller of the two multiplets, which may be assigned to the methylene protons of the phosphine trans to the halogeno-ligand. Both methylene multiplets shift downfield on halogen change, although the degree of deshielding is greater (Table 3.4) for the smaller area multiplet (phosphine trans to halogen) than for the larger area multiplet (phosphine trans to phosphine). This may be related to the stronger metal-phosphorus bond for the phosphine trans to the halogeno-ligand. The downfield shifts, with halogen

TABLE 3.5

^{13}C NMR Spectra of Rhenium (V) Oxo Complexes[a]

Compound	methyl	methylene	C_1	C_{ortho}	C_{meta}	C_{para}
cis-$ReOCl_3(Et_2PhP)_2$	-7.22s	-19.62 t (35.0)		-131.14s	-128.72d(3.6)	-130.66s
trans-$ReOCl_3(Et_2PhP)_2$	-7.03s	-15.53 t (29.6)		-131.61 t (7.6)	-128.70 t (6.0)	-130.66s
trans-$ReOBr_3(Et_2PhP)_2$	-7.47s	-16.25 t (32.0)	-129.38 s (c)	-131.77 t (4.0)	-128.28 t (4.4)	-130.72s
cis-$ReOCl_3(PEt_3)_2$	-8.01s	-19.53 (b)(31.6)				
trans-$ReOCl_3(PEt_3)_2$	-7.22s	-15.33 t (30.6)				
trans-$ReOBr_3(PEt_3)_2$	-7.42s -7.51s	-16.21 t (28.0) -16.99 t (28.0)				

(a) s = singlet; d = doublet; t = triplet
resonances in ppm downfield from TMS
coupling constants (Hz) in parentheses

(b) "filled-in" doublet (see text and Fig. 3.3)

(c) observed on addition of $Cr(acac)_3$

change, for both multiplets can be rationalised using similar explanations as advanced for square planar complexes (Chapter 2) and rhenium (V) oxo complexes.

The phenyl region of the spectra shows two separate resonance areas. The smaller of the two resonances at lower field is assigned to the ortho protons, as before.

The complex, $ReNBr_2(Et_2PhP)_3$, gives a spectrum in which multiplet structure is not well resolved. This could be the result of some paramagnetic impurity. However, repeated recrystallisation did not improve the quality of the spectrum.

(c) ^{13}C NMR spectra of oxo complexes :-

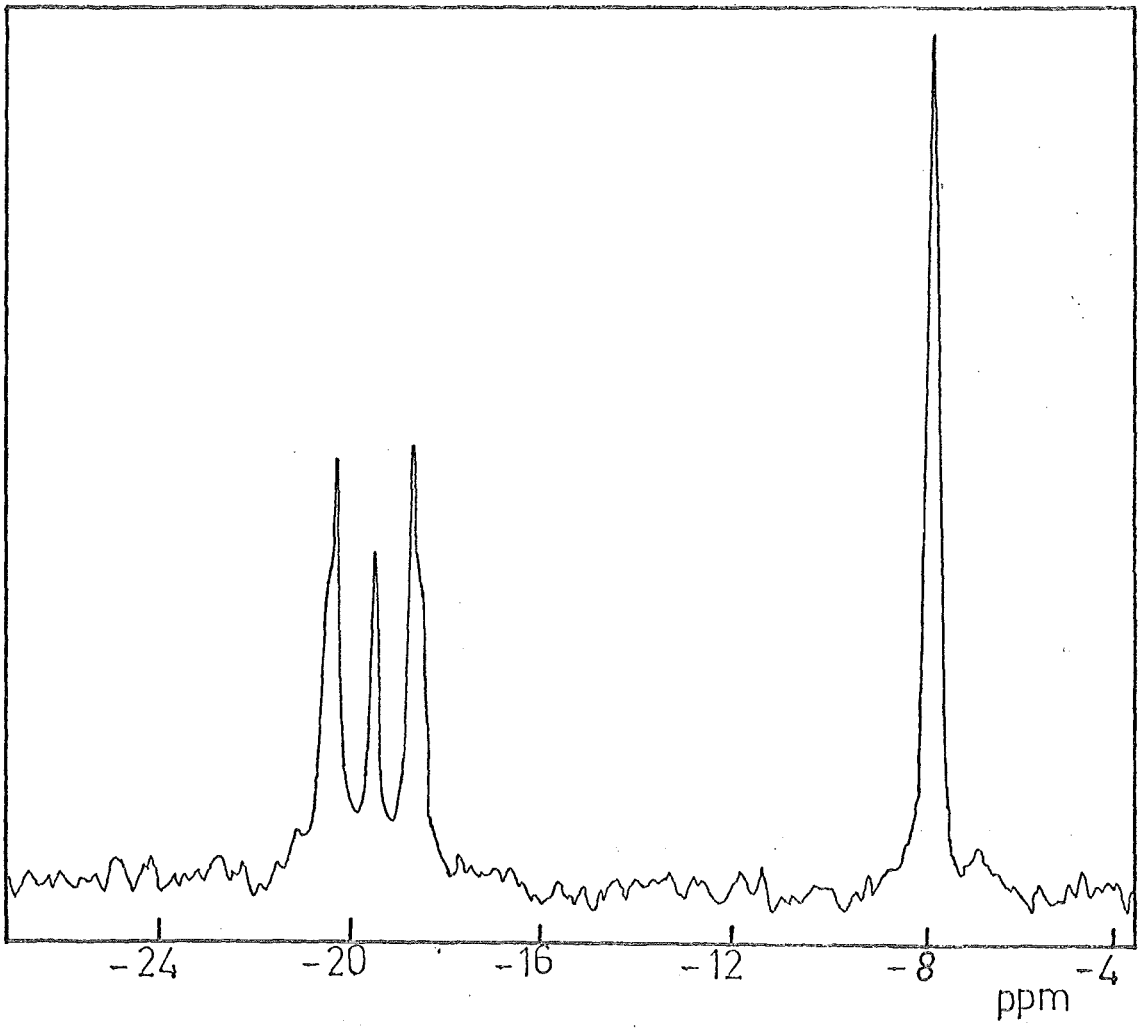
The ^{13}C NMR spectra of the four chloro and two bromo rhenium (V) complexes with oxo ligands have been obtained. The quality of the spectra of PEt_3 complexes is considerably better than that of the Et_2PhP compounds. Only poorly resolved spectra could be obtained for the nitrido complexes and they are not further discussed.

Assignment of spectra

The spectrum of the complex cis-$ReOCl_3(PEt_3)_2$ provides a good example of the caution necessary in interpreting ^{13}C NMR spectra, as previously discussed in Chapter 2. Thus the complex, which is considered to have a cis arrangement of phosphine ligands, does not show the doublet for the methylene multiplet which might be expected on the basis of lack of virtual coupling for phosphine nuclei cis to each other. However, Carey et al.[74] have pointed out that the very low natural abundance of the ^{13}C isotope of carbon causes a change in spin system for these compounds (see earlier discussion,

FIGURE 3·3

^{13}C NMR SPECTRUM OF CIS $ReOCl_3(PEt_3)_2$



Chapter 2) and one of the consequences of this is that a triplet will be observed for ^{31}P- ^{13}C coupling at much lower values of Jpp' than is the case in proton spectra. These workers also showed, by use of computer simulation of a range of spectra calculated by varying the value of Jpp' that as this coupling constant nears zero the observed triplet collapses, first to a "filled-in" doublet and finally to a single doublet when Jpp' is less than the resolving power of the spectrometer.

The spectrum of cis-$ReOCl_3(PEt_3)_2$ obtained in this work (Figure 3.3) is a good example of a filled-in doublet. Carey et al.[74] observed a similar multiplet using computer simulation techniques when Jpp' = 10 Hz . Also these workers observed a triplet of intensity ratio 1:2:1 for Jpp' = 500 Hz , a typical case of virtually coupled trans phosphine nuclei, and a doublet when Jpp' = 0 Hz , as found for cis phosphine environments where the P-M-P angle is 90°. [74] Thus in the case of the cis-$ReOCl_3(PEt_3)_2$ complex studied in the present work it appears likely that the observed multiplet structure arises from a small but non-zero phosphorus-phosphorus coupling constant, and that this in turn is non-zero because the P-M-P' angle is distorted from 90°. Thus this result may be a natural reflection of the lowered symmetry in the complex, and multiplet shape might thus be used as an approximate measure of distortion.

The spectrum of the complex trans-$ReOBr_3(PEt_3)_2$ can be assigned on the basis of two marginally different phosphine environments. The methylene multiplets consist of four lines arising from overlap of two triplets with different chemical shifts. Two singlet methyl resonances are also observed. The presence of two slightly different phosphine environments may reflect the influences of non-bonded interactions in the complex.

If the complex had the structure shown in Figure 3.1(c) (see earlier discussion) the difference between the two phosphine environments as measured by the difference in NMR chemical shifts for the methyl and methylene multiplets could reasonably be expected to be larger than is observed here (Table 3.5).

The phenyl region of the spectra of the Et_2PhP complexes shows the resonances of three types of carbon atoms (Table 3.5). The resonance of the C_1 carbon is observed only in the bromo complex. For the cis- and trans- chloro complexes the relaxation time is presumably too long for this absorption to be observed and the addition of the relaxation agent, $Cr(acac)_3$, (see earlier discussion, Chapter 2) does not make the C_1 peak discernible from the background noise. The ortho, meta and para carbon resonances are assigned in the same way as previously discussed for the ^{13}C spectra of square planar Et_2PhP complexes (Chapter 2). Again, the para carbon resonance is observed as a singlet while the meta and ortho carbons give rise to triplets through coupling with ^{31}P for the trans complexes, For cis-$ReOCl_3(Et_2PhP)_2$ the spectrum is not well resolved and the form of the multiplets for ortho and meta carbons is an approximate doublet, as might be expected with the lack of virtual coupling for cis phosphorus nuclei.

Trends in the spectra

The deshielding of the methylene carbon is greater for the cis isomer as compared with the trans, in the chloro complexes. This further emphasises the probability of higher rhenium-phosphorus bond strength in the cis isomer relative to the trans, as discussed previously for a similar situation observed in the ^1H NMR spectra of these complexes.

The deshielding phenomenon with change in halogen is

TABLE 3.6

Electronic Spectra of Rhenium (V) Oxo Complexes [a]

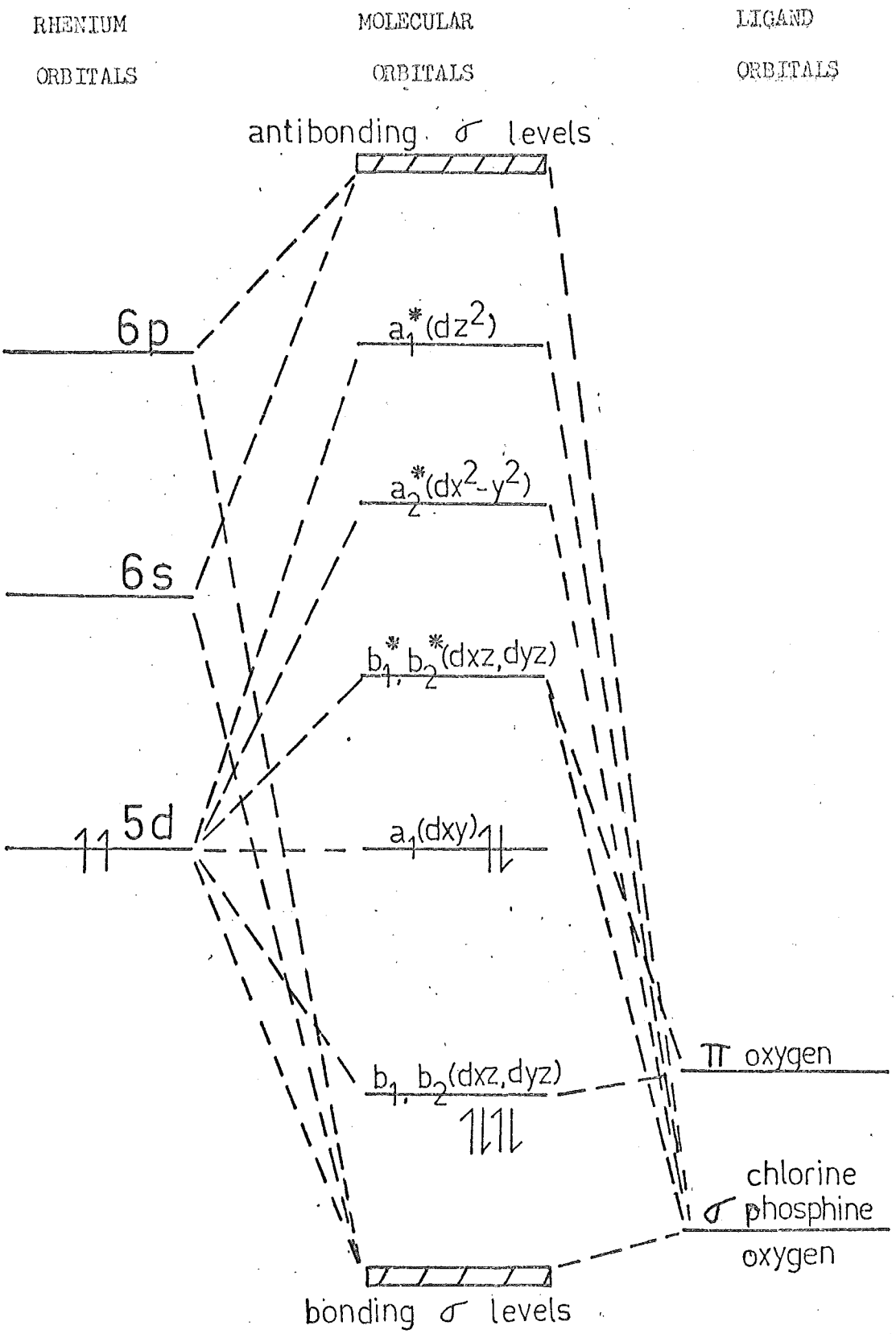
Compound	Ligand field $a_1 \rightarrow b_1^*, b_2^*$ $a_1 \rightarrow a_2^*$	oxygen $\rightarrow$ metal (a_2^*)	oxygen $\rightarrow$ metal (b_1^*, b_2^*)	phospine $\rightarrow$ metal	Other bands
cis-$ReOCl_3(Et_2PhP)_2$	590 (50)	301 sh (3900)	365 sh (1300)	252 sh (10,300)	
cis-$ReOCl_3(PEt_3)_2$	602 (65)	303 (4400)	(b)	(b)	
trans-$ReOCl_3(Et_2PhP)_2$	405sh(620) 610 (27)	300 sh (3200)	361 sh (980)	251 sh (6900)	
trans-$ReOCl_3(PEt_3)_2$	390sh(630) 680 (38)	(b)	360 (780)	269 sh (5000)	289sh (2500)
trans-$ReOBr_3(Et_2PhP)_2$	437sh(450) 600 (20)	310 sh (3200)	357 sh (2200)	270 sh (13,500)	
trans-$ReOBr_3(PEt_3)_2$	428sh(370) 690 (40)	306 (2900)	362 sh (2000)	247 (8100)	
$ReOI_3(Et_2PhP)_2$	640 (80) 539 (165) 414sh(800)	(b)	(b)	282 (9200)	332 sh (3000)
$ReOI_3(PEt_3)_2$	(b)	(b)	(b)	278 sh (6700)	395 sh (1250)

(a) Extinction coefficients in parentheses
Wavelength in nanometres
sh = shoulder

(b) no absorption assignable

FIGURE 3·4

ENERGY LEVEL DIAGRAM FOR RHENIUM(V) OXO COMPLEXES



Labels for trans complexes (C_{2v} symmetry)

again apparent in the ^{13}C spectra of these complexes and may be rationalised in the same way as discussed before. The degree of deshielding is less here for these d^2 complexes than halogen change causes in the d^8 square planar complexes. This gives support to the metal-halogen $M_{d\pi} \longrightarrow X_{d\pi}$ bonding explanation, discussed in Chapter 2 and for the ^1H NMR spectra of oxo and nitrido complexes previously considered in this Chapter. A more extensive discussion is delayed until Chapter 5.

(iii) Electronic absorption spectra of Rhenium (V) complexes Electronic absorption spectra have been recorded for the complexes in the ultra-violet and visible regions in chloroform solution. Methanol could not be used because of solubility problems. There are four general areas of absorption in the spectra of these complexes and assignments have been made as in Tables 3.6 and 3.7.

(a) Spectra of the oxo complexes :-

The molecular orbital energy level diagram given in Figure 3.4 is useful when making assignments for spectra of the oxo complexes. This diagram is based on that of Gray and Hare[167] for $[MOCl_5]^{2-}$ complexes of chromium and molybdenum, where the metal ion has the d^1 configuration, and this electron is considered[167] to occupy the d_{xy} orbital (b_2 symmetry label). In the case of the rhenium (V) oxo complexes (d^2 configuration) studied here the a_1 type orbital may be considered to accommodate both electrons, as discussed previously.

There are three possible ligand field transitions for these complexes (Figure 3.4). (There will be four possible transitions if the degeneracy of the d_{xz} and d_{yz} orbitals is lifted). The broad bands observed in the spectra have two

resolvable components (Table 3.6), the higher energy component also having the higher extinction coefficient. The low energy band may correspond to a transition to a relatively low-lying empty orbital, probably one of the b_1^*, b_2^* (d_{xz} , d_{yz}) orbitals. The higher energy band could correspond to a transition to either the a_2^* ($d_{x^2-y^2}$) or a_1^* (d_{z^2}) orbital. (The symmetry labels given here are for <u>trans</u> complexes, C_{2v} symmetry. The <u>cis</u> complexes have C_s symmetry with orbital labels as in Figure 3.4).

There are generally three regions of charge transfer absorption in the spectra, although for some spectra all three types are not observed (Table 3.6). The spectra appear to be dominated by transitions involving the oxo ligand. Thus two bands may be readily assigned to transitions from this ligand to the metal ion. These occur at around 300 nm and 360 nm respectively. The lower energy transition may be considered to terminate on the b_1^*, b_2^* (d_{xz} , d_{yz}) orbitals, and the higher energy transition could terminate on the a_2^* ($d_{x^2-y^2}$) orbital. Halogen to metal charge transfer transitions, if they occur, can be expected in this general region. However, the bands discussed here show little variation with change in halogen, at least for chloro and bromo complexes.

A third region of charge transfer absorption occurs around 260 nm (Table 3.6). For this band there is some change in energy with change in halogen ; however, this change is not systematic. The band could correspond either to a third type of oxygen to metal charge transfer transition (to the a_1^* (d_{z^2}) orbital) or to a phosphine - metal charge transfer transition. Gray and Hare[167] consider that this third possible type of oxygen to metal charge transfer will be at very high energy and hence the assignment to a phosphine-metal charge transfer has been made

TABLE 3.7

Electronic Spectra of Rhenium (V) Nitrido Complexes [a]

Compound	Ligand field	nitrogen→metal	phosphine—metal	nitrogen→metal or intraligand
$ReNCl_2(Et_2PhP)_3$	428 (340) 351 (720)	(b)	(b)	292 sh (2800)
$ReNBr_2(Et_2PhP)_3$	460 (900)	399 (1500) 335 (2500)	245 (21,000)	291 sh (3500)
$ReNI_2(Et_2PhP)_3$	451 (195)	(b)	251 (15,500)	(b)

(a) Extinction coefficients in parentheses
Wavelength in nanometres
sh = shoulder

(b) no absorption assignable

in the present work. For the free phosphine ligands diethylphenylphosphine has an absorption at 290 nm but triethylphosphine has no absorptions in the range 220-1200 nm. Because the band near 260 nm is present in the spectra of both Et_2PhP and PEt_3 complexes then assignment to an intra-ligand transition is not feasible.

(b) Spectra of the nitrido complexes :-

The electronic spectra of the nitrido complexes show a number of inconsistencies which make interpretation difficult. The only common features in the spectra of all three complexes are the ligand field transitions (Table 3.7).

The relative ordering of the energy levels in the nitrido complexes can be expected to be similar to that of Figure 3.4 for the oxo complexes. The ligand field bands are broad and appear to consist of several components, as can be expected on the basis of Figure 3.4. The low energy weak band present in the spectra of the oxo complexes has not been observed in the nitrido spectra.

The charge transfer region of the spectra has three general regions of absorption none of which is observed for all three complexes (Table 3.7). Thus for the chloro and bromo complexes a shoulder near 290 nm in both spectra can be assigned to a transition from the nitrido ligand to the metal ion, mainly by analogy with the spectra of the oxo complexes, but also because the band does not vary with change in halogen. There is some possibility that the band could correspond to an intra-ligand transition of the Et_2PhP ligand, however.

The band in the bromo and iodo spectra near 250 nm may be assigned to a phosphine to metal charge transfer transition

again by analogy with the oxo complexes.

Only the bromo complex has other absorptions. Thus two bands at 399 and 335 nm are observed in the spectrum of this complex. It is not possible to make an assignment for these bands with any confidence since similar bands are not observed for the chloro and iodo complexes. However it can be tentatively suggested that, again by analogy with the spectra of the oxo complexes, the bands could correspond to lower energy nitrido to metal charge transfer transitions.

3.1.3 Experimental

(a) Preparation of Rhenium (V) oxo complexes :-

Oxotrichlorobis(triphenylphosphine)rhenium(V),[153] $ReOCl_3(Ph_3P)_2$

Sodium perrhenate (1.46gm), concentrated hydrochloric acid (10ml) and ethanol (40ml) were boiled under reflux. To this mixture was added triphenylphosphine (8gm) in hot ethanol (40ml). A yellow precipitate formed almost immediately and the solution was heated under reflux for a further hour, filtered hot and washed with ethanol. The yellow-green powdery product was dried in vacuo, (3.9gm, 87%). m.pt. 211-212° c f.lit.[168] 211-214°.

Cis- and Trans- oxotrichlorobis(triethylphosphine) rhenium(V),[150] $ReOCl_3(PEt_3)_2$

$ReOCl_3(Ph_3P)_2$, as prepared above, (1gm) was suspended in benzene (150ml) and the suspension was treated with PEt_3 (0.58gm). The flask was flushed with nitrogen, sealed, and kept for 20 hours at room temperature. At the end of this time the solution was a clear emerald green in colour. The solution was transferred to a 250ml separatory funnel and

washed with concentrated hydrochloric acid (4x50ml) to remove excess of PEt_3 and also displaced Ph_3P. Further washing with distilled water (4x75ml) removed any residual hydrochloric acid and the solution was then dried over anhydrous sodium sulphate. Evaporation to dryness at 15mm gave a mixture of blue and green crystals, corresponding to the cis and trans isomers respectively of the required complex. The trans complex was dissolved by addition of ether and the cis isomer filtered off. Recrystallisation from acetone gave bright blue needles (0.27gm, 41%). m.pt. 122-125°, c.f.lit.[153] 126-129°. ν(Re-O) at 980 cm^{-1} c.f. lit.[153] 982 cm^{-1}. Analysis : Calculated for $C_{12}H_{30}Cl_3OP_2Re$, C = 26.4%; H = 5.50%. Found : C = 26.3%; H = 5.48%. Slow evaporation of the green ether extract deposited large prisms of the trans isomer (0.20gm, 31%) m.pt. 166-171° c.f. lit.[153] 164-174°. ν(Re-O) at 977 cm^{-1} c f. lit.[153] 973 cm^{-1}. Analysis : Calculated for $C_{12}H_{30}Cl_3OP_2Re$, C = 26.4%; H = 5.50%. Found : C = 26.8%; H = 5.37%.

cis-oxotrichlorobis(diethylphenylphosphine)rhenium(V),[153] $ReOCl_3(Et_2PhP)_2$

Method (i) [153] : A similar preparation to that outlined above for the triethylphosphine complex gave blue needles of cis-$ReOCl_3(Et_2PhP)_2$ (yield 37%). m.pt. 155-158° c f.lit.[153] 157-160°. ν(Re-O) at 978 cm^{-1} c f. lit.[153] 977 cm^{-1}. Analysis : Calculated for $C_{20}H_{30}Cl_3OP_2Re$, C = 37.4%; H = 4.68%. Found : C = 37.7%; H = 4.67%. Attempts to obtain the trans isomer using this ligand displacement method were not successful, leading only to brown-green oils.

Method (ii) [153] : Sodium perrhenate (0.6gm), Et_2PhP (1.8gm), concentrated hydrochloric acid (4ml), and

ethanol (40ml) were boiled together under reflux for 4 hours. The green-brown solution was concentrated to 15ml volume with accompanying precipitation of a purple-blue solid. The purple colour was extracted by shaking with benzene. The blue compound remaining was filtered off to give the required cis isomer. The mother liquor was set aside and a further quantity of cis isomer slowly precipitated. (0.35gm, 25%). Again no trans isomer could be obtained in crystalline form from ether extracts of the mother liquor.

Trans-oxotrichlorobis(diethylphenylphosphine)rhenium(V)[153], $ReOCl_3(Et_2PhP)_2$

The cis isomer (from (i) or (ii) above) was dissolved in 2-ethoxyethanol (5ml) and heated to the boiling point. The solution slowly turned green during the procedure and after evaporation of the solvent the green trans isomer was obtained (0.15gm, 50%). m.pt. 164-167° c f. lit.[153] 166-169°. ν(Re-O) at 977 cm^{-1} c f. lit.[153] 978 cm^{-1}. Analysis : Calculated for $C_{20}H_{30}Cl_3OP_2Re$, C = 37.4%; H = 4.68%. Found : C = 38.1%; H = 5.03%.

Trans-oxotribromobis(diethylphenylphosphine)rhenium(V)[150], $ReOBr_3(Et_2PhP)_2$

Method (i)[150] : Sodium perrhenate (0.3gm), concentrated hydrobromic acid (2.5ml), Et_2PhP (0.7gm) and ethanol (30ml) were boiled together under reflux for 7 hours. The brown solution so formed was evaporated to give an oil. Trituration of this with ice-cold methanol (1ml) gave a yellow-green solid; the green colour was extracted by shaking with chloroform. Addition of light petroleum (50-70) to this solution caused the deposition of green crystals of the required complex which were recrystallised

from dichloromethane/light petroleum (50-70), (0.39gm, 46%). m.pt. 168-172° c f. lit.[150] 171-175°. ν(Re-O) at 999, 978 cm^{-1} c f. lit.[150] 997,977 cm^{-1}. Analysis : Calculated for $C_{20}H_{30}Br_3OP_2Re$, C = 31.0%; H = 3.88%. Found : C = 31.9%; H = 4.33%.

Method (ii) : A metathetical preparation analogous to that described below for the PEt_3 complex gave the compound in 48% yield.

Trans-oxotribromobis(triethylphosphine)rhenium(V), $ReOBr_3(PEt_3)_2$

The trichloro analogue of the required compound (0.2gm) was dissolved in acetone (30ml) containing lithium bromide (2gm). This mixture was boiled under reflux for 15 minutes during which time the bright blue solution changed to emerald green. The solution was taken to dryness at 15mm and extracted with chloroform. This extract was washed with water and dried over anhydrous sodium sulphate. Addition of light petroleum (50-70) followed by a period in the cold room lead to the precipitation of green crystals of the required compound (0.18gm, 72%). m.pt. 135-137°. ν(Re-O) at 978 cm^{-1}. Analysis : Calculated for $C_{12}H_{30}Br_3OP_2Re$, C = 21.2%; H = 4.42%. Found : C = 22.3 %; H = 4.73%.

Oxotriiodobis(diethylphenylphosphine)rhenium(V)[153], $ReOI_3(Et_2PhP)_2$

A similar metathetical reaction to that used in the preparation of trans-$ReOBr_3(PEt_3)_2$, with sodium iodide in place of lithium bromide, gave the required complex as brown needles (58%). m.pt. 165-168°. c f. lit.[153] 171.5 - 174°. ν (Re-O) at 976 cm^{-1} c.f. lit.[153] 976 cm^{-1}. Analysis : Calculated for $C_{20}H_{30}I_3OP_2Re$, C = 26.2%; H = 3.28%. Found : C = 26.6%; H = 3.46%.

Oxotriiodobis(triethylphosphine)rhenium(V),

$ReOI_3(PEt_3)_2$

The preparation was analogous to that for the diethylphenylphosphine complex above. The complex was recovered as brown microcrystals (74%) from light petroleum (80-100) m.pt. 125°. ν (Re-O) at 977 cm^{-1}. Analysis :Calculated for $C_{12}H_{30}I_3OP_2Re$, C = 17.6%; H = 3.66%. Found : C = 17.4%; H = 3.44%.

(b) Preparation of Rhenium (V) nitrido complexes :-

Nitridodichlorobis(triphenylphosphine)rhenium(V),[153]

$ReNCl_2(Ph_3P)_2$

Hydrazine dihydrochloride (0.5gm) in water (2ml) and Ph_3P (2.7gm) in hot ethanol (80ml) were added in that order to a solution of sodium perrhenate (0.5gm) in hydrochloric acid (0.5 N, 5ml). The reaction mixture was heated to the boiling point and benzene (130ml) added dropwise. The mixture was simultaneously distilled during this addition to remove the benzene-ethanol-water azeotrope. No visible reaction had occurred until almost all the azeotrope had been removed when a brown precipitate was formed rapidly. This was filtered off, washed with ethanol and dried in vacuo. (0.94gm, 65%).

Nitridodibromobis(triphenylphosphine)rhenium(V),[161]

$ReNBr_2(Ph_3P)_2$

Using hydrazine dihydrobromide and hydrobromic acid in place of their chloro analogues in the above preparation gave the required nitridodibromo complex as brown microcrystals (61%).

Nitridodiiodobis(triphenylphosphine)rhenium(V)[161],

$ReNI_2(Ph_3P)_2$

(i) Rhenium heptoxide was prepared by heating rhenium metal in a glass tube filled with oxygen. The heptoxide condensed on the walls of the tube as yellow needles which were taken up in ethanol.

(ii) Hydriodic acid (55%, 1ml) was added to hydrazine hydrate (0.2ml) in ethanol (10ml). This was mixed with a solution of Ph_3P (2gm) in ethanol (30ml) and benzene (20ml) was added. The mixture was slowly distilled with dropwise addition of ethanol (20ml) until the residual volume was 20ml. A solution of rhenium heptoxide (0.4gm) in ethanol was added dropwise and the solution changed to a red-brown colour. The mixture was refluxed for 1 hour and then filtered hot to give maroon crystals of the nitridodiiodo complex (0.42gm, 50%).

Nitridodichlorotris(diethylphenylphosphine)rhenium(V)[161], $ReNCl_2(Et_2PhP)_3$

$ReNCl_2(Ph_3P)_2$ (0.5gm) was treated with Et_2PhP (1.2gm) in boiling benzene (70ml). The solution was refluxed for 20 hours, then cooled and evaporated at 15 mm to give a yellow-brown oil. Treatment of the oil with ether (20ml) and standing the mixture in the cold room overnight lead to the formation of a yellow crystalline solid. This was filtered off and washed with light petroleum (50-70) to give mustard yellow microcrystals (0.13gm, 30%). m.pt. 150-151° c f. lit.[161] 151-154°. ν (Re-N) at 1048 cm^{-1} c f. lit.[161] 1052 cm^{-1}. Analysis : Calculated for $C_{30}H_{45}Cl_2NP_3Re$, C = 46.8%; H = 5.85%. Found : C = 46.5%; H = 5.80%.

Nitridodibromotris(diethylphenylphosphine)rhenium(V)[161], $ReNBr_2(Et_2PhP)_3$

An analogous preparation to that above for the dichloro

complex, and using $ReNBr_2(Ph_3P)_2$ (0.5gm) gave yellow microcrystals of the required compound (0.2gm, 41%). m.pt. 146-149° c f. lit.[161] 151-155°. ν(Re-N) at 1050 cm^{-1} c f. lit.[161] 1052 cm^{-1}. Analysis : Calculated for $C_{30}H_{45}Br_2NP_3Re$, C = 42.0%; H = 5.24%. Found : C = 42.4%; H = 5.05%.

Nitridodiiodotris(diethylphenylphosphine)rhenium(V),[161] $ReNI_2(Et_2PhP)_3$

An analogous preparation to that for the dichloro complex but using $ReNI_2(Ph_3P)_2$ (0.42gm) gave, again, yellow microcrystals (0.21gm, 52%). m.pt. 112-116° c f. lit.[161] 115-118°, ν(Re-N) at 1052 cm^{-1}. Analysis : Calculated for $C_{30}H_{45}I_2NP_3Re$, C = 37.8%; H = 4.72%. Found : C = 37.2%; H = 4.80%.

Attempted preparation of nitridodihalogenotris (triethylphosphine)rhenium(V) complexes[161] :-

Dichloro complex :- $ReNCl_2(Ph_3P)_2$ (0.5gm) was treated with PEt_3 (1.0gm) in boiling benzene (75ml) and the mixture was refluxed for 21 hours. The brown-red solution was evaporated to 25ml and chromatographed using 10% deactivated H grade alumina. The column was washed with benzene (200ml) to remove free phosphines and the product was eluted with ethanol-benzene (1:20, 70ml). The result was a brown oil which could not be crystallised. Further attempts using 15% deactivated alumina and silica (Sorbsil) as chromatographic materials, and elution with a variety of solvents all led to decomposition.

Dibromo complex :- An attempt to prepare the dibromo complex by the above method was also fruitless.

SECTION 3.2. SOME ASPECTS OF THE CHEMISTRY OF RHENIUM HALOGENO-PHOSPHINE NITROSYL COMPLEXES

The work described in this section is concerned with the preparation of some rhenium halogeno-phosphine nitrosyl complexes and the study of these complexes by spectroscopic techniques. The communicated results of X-ray crystallographic studies have also been considered, and some general chemistry of the compounds has been investigated.

3.2.1 Introduction

Mono-nitrosyl complexes of rhenium containing phosphine ligands were, until recently, the exception rather than the rule. Giusta and Cova[169] prepared the complexes, $ReX_3(NO)(Ph_3P)_2$ (X = Cl,Br), by reaction of the appropriate pentahalogenonitrosylrhenate salt with Ph_3P under reflux in ethanol. Sen et al.[170,171] have prepared $ReCl_3(NO)$ and $ReBr_3(NO)$ and have formed pyridine adducts, $ReX_3(NO)L_2$, from them.[172]

Chatt et al.[173] recently reported the preparation of $ReCl_3(NO)L_2$ (L = tertiary phosphine) by bubbling nitric oxide through a benzene solution of $ReCl_3L_3$ heated under reflux. These workers also prepared $ReCl_2(NO)L_3$ complexes which are diamagnetic[173], and in which the Re-N-O group is linear.[174]

(a) Bonding in nitrosyl complexes :-

The bonding in metal nitrosyl complexes has recently been reviewed in some detail[175,176]. For many years it was felt that the mode of coordination of nitric oxide in metal complexes was linear[177] and it was not until the first structural determination concerning a bent M-N-O unit[178] that there was

any definite evidence to refute this view. Since 1967 however a number of complexes containing bent M-N-O groups have been reported[175,176] and bonding theories of the metal - NO interaction have had to be extended to accommodate this second mode of nitric oxide bonding.

Neutral nitric oxide has one unpaired electron contained in an antibonding orbital and this electron is readily lost[177] to give NO^+, the nitrosonium ion, which is isoelectronic with carbon monoxide. When nitric oxide bonds to a metal ion in the linear mode the unpaired electron can be regarded as being transferred to the metal. The nitric oxide is now formally NO^+. This ion can coordinate by donation of an electron pair into an empty metal orbital. Thus nitric oxide is formally a three electron donor in this situation. In the case of bent M-N-O groups the metal may be considered to donate an electron to nitric oxide, giving rise to the NO^- ion. This produces a change in hybridisation about nitrogen (sp^2) and the subsequent electron pair donation results in a bent M-N-O linkage, with bond angles ranging from 120 - 130° in general. In this situation nitric oxide is regarded as formally a one electron donor.

The above description, while not rigorous, leads qualitatively to the same findings as arrived at by molecular orbital approaches[175,176]. Overall, the linear mode of bonding by NO^+ leads to a lowering of the metal formal oxidation state by one unit, and coordination of NO^- results in an increase in formal oxidation state by one unit. Thus X-ray single crystal structural studies are the most reliable method of determining the formal oxidation states of metal ions in nitrosyl complexes, if such data cannot be determined unambiguously from spectroscopic measurements.

(b) The occurrence of rhenium (II) :-

The divalent oxidation state is the most poorly characterised of the eight oxidation states of rhenium[157,179]. Many compounds which have originally been considered as complexes of rhenium (II) have on later study been shown to contain other oxidation states of rhenium[157]. The few well characterised compounds of rhenium (II) is perhaps surprising in view of the common occurrence of other metal ion complexes with the d^5 configuration, such as W(I), Os(III) and Ru(III).

The best characterised complexes of rhenium (II) are those containing polydentate arsine ligands[157,180,181] and complexes with dinitrogen as a ligand[182]. Other compounds claimed to contain Re(II) are less well characterised[157,179].

3.2.2 Results and Discussion

(a) Preparative Studies :-

The methods of Giusta and Cova[169] and of Sen and co-workers[170-172] appeared to be likely preparative routes to the preparation of $ReX_3(NO)L_2$ species, where L is PEt_3 or Et_2PhP. However, these two preparative methods and modifications of them, in the present work failed to yield compounds of the expected composition. The reaction of $ReBr_3(NO)$ (prepared according to the method of the Indian workers[171]) and Et_2PhP gave instead the yellow diamagnetic complex, $ReBr_2(NO)(Et_2PhP)_3$. Attempts to prepare the analogous chloro complex by this same method were unsuccessful.

Reaction of the pentachloronitrosylrhenate anion with PEt_3 or Et_2PhP in ethanol[169] boiling under reflux gave no identifiable products. When the solvent was DMF a yellow

solution resulted. However, no crystalline product could be obtained from this solution.

While this work was in progress Chatt et al.[173] reported the preparation of $ReCl_3(NO)L_2$ and $ReCl_2(NO)L_3$ complexes. The $ReCl_3(NO)L_2$ compounds were prepared by bubbling nitric oxide through a benzene solution of $ReCl_3L_3$ boiling under reflux. This preparative technique has proved particularly successful in the present work and the complexes $ReX_3(NO)(Et_2PhP)_2$ (X = Cl,Br,I) have been characterised and studied.

Attempts to prepare $ReX_2(NO)L_3$ complexes by the method of Chatt and co-workers[173] were not successful. However an alternative preparation by reduction of $ReCl_3(NO)(Et_2PhP)_2$ with sulphite in ethanol boiling under reflux has been achieved. Chromatographic techniques were necessary to obtain the pure product. Reduction with hydrazine hydrate was also attempted but crystalline products could not be obtained. It seems likely that sulphite reduction of $ReX_3(NO)L_2$ is a general preparative route to $ReX_2(NO)L_3$ species, and this one step reaction has advantages over the alternative preparation devised by Chatt et al.[173], which requires a reaction sequence of several steps of rather low yield.

In view of the ease with which the nitrosylation reaction proceeds for trichlorotris(phosphine)rhenium(III)complexes, the same reaction was attempted for the tetrachlorobis(diethylphenyl phosphine)rhenium(IV) complex. However no reaction occurred even after prolonged reflux.

(b) The Structure of $ReX_3(NO)L_2$ and Related Compounds :-

It was of considerable interest in this work to determine the formal oxidation state of rhenium in the complexes, $ReX_3(NO)(Et_2PhP)_2$ (X = Cl,Br,I), prepared here. Chatt et al.[173], who originally prepared the chloro complex, did not assign an oxidation state to rhenium.

(i) Results from infra-red spectra and magnetic studies

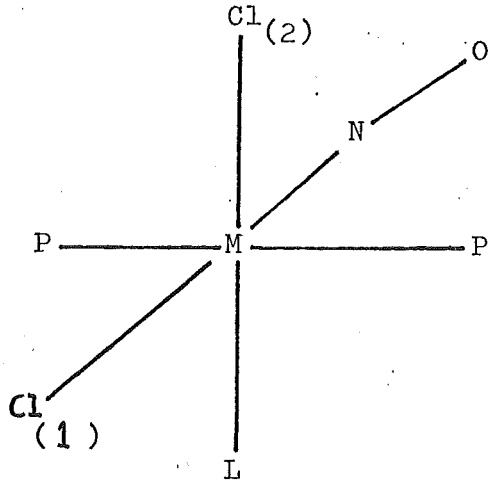
The infra-red stretching frequency of the coordinated nitrosyl ligand was once thought to be diagnostic[176] of the presence of NO^+ or NO^-. In the light of the correlation of recent structural studies with infra-red nitrosyl stretching frequencies[175,176] there appears to be considerable overlap of the two regions. The value of ν(NO) in the complex $ReCl_3(NO)(Et_2PhP)_2$ is 1735 cm^{-1} and this is in a position where it cannot be definitely assigned to either NO^+ or NO^-.

The magnetic moments of $ReCl_3(NO)(Et_2PhP)_2$ and $ReBr_3(NO)(Et_2PhP)_2$ were determined by the Gouy method at room temperature and had values of 1.82 and 2.04 B.M. respectively. This is in accord with the spin-only value for one unpaired electron which would be the situation for spin-paired rhenium (II) having a d^5 configuration, assuming the nitrosyl is coordinated as NO^+. If the M-N-O entity was bent, and hence the nitrosyl coordinated as NO^-, the rhenium would be formally in the tetravalent oxidation state and thus would have a d^3 electron configuration, with a spin-only moment of around 3.6 B.M. in an octahedral field.

(ii) Discussion of the structures of rhenium nitrosyl complexes It seemed probable from the magnetic measurements discussed above that the rhenium in

TABLE 3.8

Structural Details for some Rhenium and Ruthenium Mono-nitrosyl Complexes [a]



Compound

A M = Re, L = Cl^-

B M = Re, L = MeOH

C M = Re, L = P

D M = Ru, L = Cl^-

P = $MePh_2P$

Compound	M-P	M-Cl (1)	M-Cl (2)	M-L	M-N	N-O	M-N-O	(N-O) cm^{-1}
A [b]	250.8	232.6	235.4	235.4	194	107	175	1740
B [b]	248.3	241.3	241.2	196	172	120	171	1710
C [c]	246.3	243.9	246.6	241.4	175	117.7	178	1670, 1690
D [d]	243.5	235.7	239.8	239.8	174.4	113.2	176	1850

(a) bond lengths in pm

(b) data from ref. 183

(c) data from ref. 174

(d) data from ref. 184

$ReX_3(NO)L_2$ complexes had a d^5 electron configuration and hence was in the divalent formal oxidation state. In order to confirm this an X-ray single crystal structure determination of the complex $ReCl_3(NO)(Et_2PhP)_2$ was commenced. This work had only reached the preliminary stages when a communication was received[183] confirming that a structure determination of the $MePh_2P$ analogue had recently been completed. Muir[183] has kindly supplied data on this structure and that of the related compound, $ReCl_2(NO)(MePh_2P)_2(MeOH)$. Also a brief report of the structure of $ReCl_2(NO)(MePh_2P)_3$ has appeared recently[174]. All three structures show "only minor distortions"[183] from octahedral coordination at rhenium. The relevant structural data for these compounds and for the related ruthenium (II) complex, $RuCl_3(NO)(MePh_2P)_2$ are summarised in Table 3.8.

The major feature of the structures of the four complexes is that the M-N-O group is linear in each case. This confirms that the oxidation state of rhenium in $ReCl_3(NO)(MePh_2P)_2$, and therefore probably in $ReX_3(NO)L_2$ complexes in general, will be formally II.

Comparisons between these complexes are of considerable interest (Table 3.8). There is a significant shortening of the bonds to the chlorines (1) and (2) in the divalent metal complexes, as compared with $ReCl_2(NO)L_3$ with rhenium in the monovalent oxidation state. This may be related to the electrostatic effect of the higher oxidation state.

There is a small but significant increase in the metal-phosphorus bond length in the complex $ReCl_3(NO)(MePh_2P)_2$, which has rhenium with a d^5 electron configuration, as compared with the metal-phosphorus bond lengths in $ReCl_2(NO)(MePh_2P)_3$,(Re(I)), and

$RuCl_3(NO)(MePh_2P)_2$[104], (Ru(II)), complexes, which have the metal ion in the d^6 electron configuration. A tentative explanation for this is in terms of a decrease in the π-bond contribution for $d\pi - d\pi$ metal-phosphorus overlap in the d^5 as compared with the d^6 configuration.

The bond length changes in the M-N-O systems are also of interest. The metal-nitrogen bond in $ReCl_3(NO)(MePh_2P)_2$ is longer than in the complexes $ReCl_2(NO)(MePh_2P)_3$ and $RuCl_3(NO)(MePh_2P)_2$, a similar situation to that mentioned above for the metal-phosphorus bond lengths in these complexes. If π-bonding is important between the nitrosyl ligand and the metal ion it will be marginally greater for the higher electron configuration and hence the metal-nitrogen bond length can be expected to be shorter, as observed. This is supported by the trends observed in the nitrogen-oxygen bond lengths (Table 3.8). Since π-bonding between the metal and nitric oxide is considered to involve the overlap of filled metal d orbitals with the empty antibonding nitrosyl orbitals the N-O bond order will be lowered. This reduction in bond order will be greater in complexes having metal ions with greater numbers of t_{2g} electrons. This should be reflected structurally in increased N-O bond lengths for the d^6 complexes considered here and, conversely, shorter N-O distances for the d^5 complex. The relevant data of Table 3.8 are consistent with this explanation.

In general however, it is surprising that relatively large changes in bond lengths occur for such small changes in d electron configuration. This suggests that the above explanations in terms of π-bonding cannot be the entire answer.

TABLE 3.9

Electronic Spectral Parameters for Rhenium (II) Nitrosyl and Related Complexes (d)

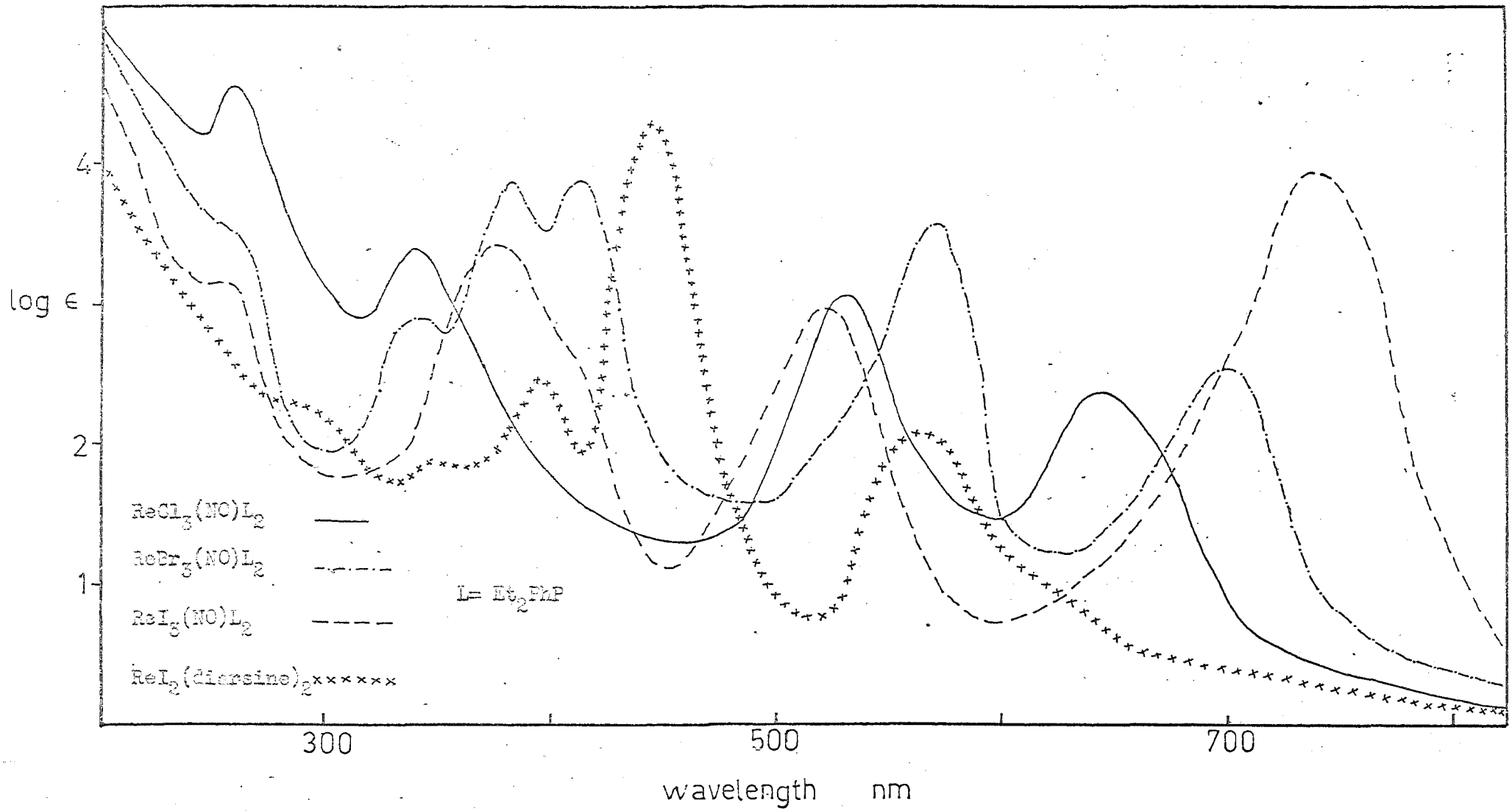
Compound	Ligand Field $^2T_2 \rightarrow {}^2A_2, {}^2T_1$	halogen→metal t_{2g}	halogen→metal e_g^*	phosphine-metal or intraligand	Other bands
$ReCl_3(NO)(Et_2PhP)_2$	640 sh (150)	524 (1000)	330 (1900)	250 (16,000)	
$ReBr_3(NO)(Et_2PhP)_2$	700 sh (300)	564 (2000)	408 (2000 372 (2000)	247 sh(18,000)	339 (1200)
$ReI_3(NO)(Et_2PhP)_2$	(a)	728 (2500)	516 (1000) 387 (1200)	247 sh(16,000)	
$ReCl_2(NO)(Et_2PhP)_3$	401 (200)	(c)	318 (2400)	251 sh(17,000)	
$ReCl_3(Et_2PhP)_3$	(b)	(b)	350 (2500)	248 (20,000)	430 (1500) 285 sh(3500)

(a) masked
(b) no absorption assignable
(c) no absorption expected

(d) wavelength in nanometres
extinction coefficients in parentheses
sh = shoulder

FIGURE 3·5

ELECTRONIC SPECTRA OF RHENIUM(II) COMPLEXES



(iii) Preliminary structural study of $ReCl_3(NO)(Et_2PhP)_2$ An X-ray single crystal structure determination of $ReCl_3(NO)(Et_2PhP)_2$ had reached the intensity data collection stage when communication[183] of the structure of the $MePh_2P$ analogue was received.

The crystal studied in the present work was monoclinic, space group $P2_{1/n}$, with unrefined unit cell dimensions $a = 940.0$, $b = 1403.1$, $c = 981.9$ pm and $\beta = 107^{\circ}\ 25^{1}$. The experimentally determined density of 1.74 gm cm^3 agreed quite well with the crystallographically calculated value of 1.76 gm cm^3, for which $Z = 2$.

(c) Spectroscopic Properties of Rhenium Nitrosyl Complexes :-

The rhenium (II) complexes, $ReX_3(NO)(Et_2PhP)_2$ (X = Cl,Br,I), have been studied in this work by far infra-red, electronic, and ^1H NMR spectroscopy. The results of these spectroscopic studies are listed in Tables 3.9 - 3.11 and some diagrammatic representations of the spectra are given in Figures 3.5 and 3.6. Comparisons with spectra obtained for the rhenium (I) complex $ReCl_2(NO)(Et_2PhP)_3$ and for $ReCl_3(Et_2PhP)_3$ have been made where applicable.

(i) Electronic absorption spectra The electronic spectra of $ReX_3(NO)(Et_2PhP)_2$ complexes have been recorded in chloroform solution in the region 240 - 1200 nm. The spectra obtained are sketched in Figure 3.5, where the absorption spectrum of the diarsine complex, $ReI_2(diarsine)_2$, is also included for purposes of comparison (see later discussion). The positions of band maxima, extinction coefficients and assignments are listed in Table 3.9.

The most noticeable feature of the spectra is the presence of an intense band at low energy. This band shifts to lower energy with change in halogen in the order Cl,Br,I and has an extinction coefficient which varies from 1100 (chloride) to 2850 (iodide). It is considered that these extinction coefficients may be rather too large to allow the band to be classified as a ligand field transition, and its assignment as a charge transfer transition seems more probable. For d^5 complexes three spin-allowed ligand field bands are possible and in these complexes a shoulder on the low energy side of the intense low energy charge transfer band noted above may correspond to the ligand field transition, $^2T_2 \rightarrow {}^2A_2$, $^2T_1$. This shoulder is not observed in the spectrum of $ReI_3(NO)(Et_2PhP)_2$, where it is probably obscured by the more intense band at 728 nm. The ligand field bands observed in the spectra of the chloro and bromo complexes are similar in both energy and intensity to bands assigned to ligand field transitions in ruthenium (III) (also d^5) systems.[185] The spectra recorded in this work have no other absorptions in the low energy region as far down as 1200 nm. Thus the intense low energy band in these spectra seems very likely to correspond to a charge transfer transition since other bands can be assigned to the expected ligand field transitions.

The observation of the charge transfer band at such low energy can be rationalised on the basis of the d^5 electron configuration of rhenium (II). There is thus a vacancy in the low lying t_{2g} orbital set and a one electron transfer from the ligands can terminate in this vacancy. This conclusion is supported by the absence of a low energy charge transfer band in the spectrum of $ReCl_2(NO)(Et_2PhP)_3$ (Table 3.9) in which the metal ion has the d^6 configuration and hence no low energy

orbital vacancy. The d^6 ruthenium (II) complexes, $RuX_3(NO)L_2$ (X = Cl,Br,I : L = PEt_3, Et_2PhP), are also devoid of charge transfer transitions in this low energy region (see Chapter 4).

The origin of the charge transfer at low energy is not so obvious however. Although, as noted above, the band shifts to lower energy with change in halogen in the order expected for a halogen to metal charge transfer transition, the energy change with change in halogen is less than that observed for the halogen to metal charge transfer band in ruthenium (III) complexes[185,186]. There may be some possibility that the charge transfer originates from the nitrosyl ligand and that change in halogen has some modification on the nitrosyl energy levels, resulting in the observed energy changes of the bands. There is no real evidence to support this possibility however.

Comparison of the spectra obtained here with those for the rhenium (II) complexes, $ReX_2(diarsine)_2$ (X = Cl,Br,I), shows a marked similarity (Fig. 3.5). A similar intense transition to that discussed above has been observed for the diarsine complexes[187], although the band is at higher energy in the diarsine case. Assignment to a halogen to metal charge transfer transition has been made[187], and this is therefore an analogous assignment to that considered probable for the rhenium (II) nitrosyl complexes under discussion. The different energies of the band in the two types of complexes may be related to the greater π-bonding ability expected for phosphine ligands as compared with the diarsine group. Metal to ligand π-bonding may be considered to stabilise the t_{2g} orbitals, and hence the lower energy transition observed for the halogeno-phosphine nitrosyl complexes of rhenium (II) may result from lowering the energy difference between halogen non-bonding electrons and the t_{2g} levels.

The narrow band widths ($\nu_{\frac{1}{2}}$ = 90 nm) of the low energy charge transfer absorption in both the diarsine and the nitrosyl complexes (Fig. 3.5) are further evidence that the transition terminates in the t_{2g} orbital set, since Fenske[188] has calculated that ligand field transitions will vibronically mix with those ligand to metal charge transfer transitions in which the final states involve the e_g^*, and not the t_{2g}, orbitals of the metal. Vibronic coupling would result in broadening of the bands and since the half-band widths noted above are of a magnitude generally considered to denote "narrow" bands, then this may be taken as evidence that the final charge transfer state involves the t_{2g} orbitals.

The spectra of the $ReX_3(NO)(Et_2PhP)_2$ complexes show two other regions of absorption which may be assigned as charge transfer transitions. A band at around 250 nm which is virtually invariant with change in halogen may be assigned to a transition involving the phosphine ligand. The free Et_2PhP ligand has a strong absorption ($\epsilon > 10^4$) at 290 nm, unlike PEt_3 (p.104) which shows no absorption in the range 220 - 1200 nm. The 250 nm band in the complexes (with $\epsilon > 10^4$) may correspond to an intraligand transition ($\pi - \pi^*$) involving the π electrons of the phenyl ring, modified upon coordination from the position of 290 nm found for the free ligand. The other possibility is that the absorption corresponds to a charge transfer transition between the phosphine and the metal.

The third region of absorption which is also probably a charge transfer band occurs between the low and high energy bands discussed above. This band varies quite considerably with change in halogen and the shift to lower energy is consistent with the decrease in electron affinity of the halogens. Thus the

TABLE 3.10

Far Infar-Red Spectra : $ReX_3(NO)(Et_2PhP)_2$ (X = Cl,Br,I) and Related Compounds

(cm^{-1})

Assignment	$ReCl_3(NO)(Et_2PhP)_2$	$ReBr_3(NO)(Et_2PhP)_2$	$ReI_3(NO)Et_2PhP)_2$	$ReCl_2(NO)(Et_2PhP)_3$	$ReCl_3(Et_2PhP)_3$
ν(Re-X) trans to NO	319s	225 vs	184 ms	293 s	306 s trans to Cl
ν(Re-X) in-plane	293ms	215 sh,m	175 wm	255 ms	256 ms trans to P
ν(Re-P)	235w	(a)	230 wm	235 wm	256 ms (see text)
X-mode	188wm	189 wm	(a)	(a)	190 w
Other bands	387w	385 w	385 m	385 m	351 w
	375 w	315 w	375 wm	330 wm	155 w,br
	145wm	162 w	325 wm	135 wm	
	110 w	112 w,br	275 w		
	65 w		148 w		
	45 w		130 w		
			90 w		

(a) masked

band can be quite reasonably assigned to a charge transfer from the halogeno-ligands to the metal ion. The higher energy of this band relative to the other probable halogen to metal charge transfer band discussed above can be related to the termination of the transition in the higher lying vacant e_g^* antibonding metal orbitals. This is further supported by the relatively broad nature of the absorptions as compared with the lower energy band assigned to halogen to metal charge transfer to the t_{2g} orbitals. Fenske's calculations[188], which show that vibronic coupling will occur for transitions to e_g^* orbitals, are thus a further justification for assigning the final state of the higher energy halogen to metal charge transfer transition as the e_g^* orbital set.

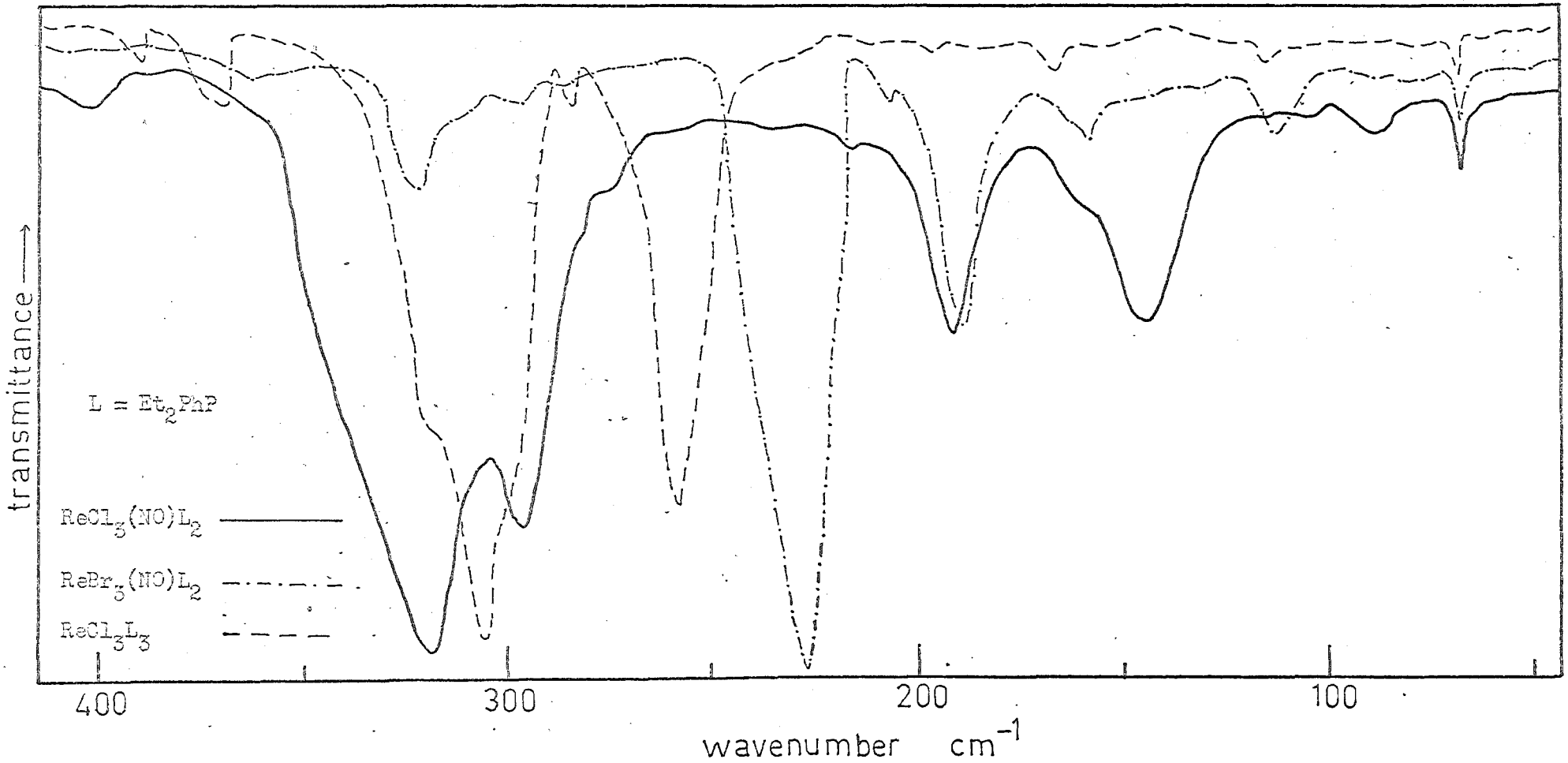
The charge transfer transitions discussed above are of the metal reduction type. This is not surprising in view of the ease of reduction of $ReCl_3(NO)(Et_2PhP)_2$ to $ReCl_2(NO)(Et_2PhP)_3$ (p. 128).

(ii) Far infra-red spectra The metal-chlorine stretching vibrations for $ReCl_3(NO)(Et_2PhP)_2$ have been observed by Chatt et al.[173] at 317 and 290 cm^{-1}. These values agree well with those found here at 319 and 293 cm^{-1}, (Table 3.10). The Re-Cl bond trans to the nitrosyl is shorter (Table 3.8) than the in-plane bonds. This implies a stronger Re-Cl bond trans to nitrosyl and hence the higher energy absorption is assigned to ν(Re-Cl) trans to nitrosyl. A weak absorption at 235 cm^{-1} could correspond to the metal-phosphorus stretching vibration, and the medium intensity absorption at 188 cm^{-1} to a Whiffen X-mode[108] (see Chapter 2).

The bromo complex has a curious spectrum consisting of

FIGURE 3·6

FAR INFRA-RED SPECTRA OF RHENIUM(II) AND (III) COMPLEXES



a very strong band at 225 cm^{-1}, a medium intensity shoulder at 215 cm^{-1}, a further band at 189 cm^{-1}, and a virtual lack of any further absorptions of even weak intensity. The 189 cm^{-1} absorption may correspond to an X-mode (Chapter 2), while the strong band and shoulder are very likely to be the two rhenium-bromine stretching vibrations. The rhenium-phosphorus stretching vibration cannot be assigned for the bromo complex since the expected absorption position is dominated by the very strong rhenium-bromine stretching vibration at 225 cm^{-1}.

The spectrum of $ReCl_2(NO)(Et_2PhP)_3$ has the metal-chlorine stretching vibrations at lower energies than for the rhenium (II) nitrosyl analogue (Table 3.10). This can be correlated with the longer Re-Cl bonds and lower Re-Cl bond strength in the rhenium (I) complex, these factors themselves arising from the electrostatic effect of the low oxidation state as compared with the situation for the rhenium (II) complex.

The spectrum of the rhenium (III) complex $ReCl_3(Et_2PhP)_3$, which has a meridional arrangement of ligands[166,189], shows two very strong absorptions at 306 cm^{-1} and 256 cm^{-1}. The higher-lying of these has been assigned previously[166] to the stretching vibration of the in-plane Cl-Re-Cl group and the other band to the Re-Cl stretching vibration trans to the phosphine ligand. That these assignments can be made in this manner is questionable on the basis of the higher oxidation state of rhenium in this complex. It might be expected that the rhenium-chlorine stretching vibrations would be found at rather higher energy for a rhenium (III) complex. In any case the very broad band centred at 256 cm^{-1} seems likely to contain two components, one being ν(Re-Cl) trans to the phosphine, and the other the rhenium-phosphorus stretching vibration.

TABLE 3.11

^{1}H NMR Spectra of Some Rhenium (II) and (III) Complexes [a]

Assignment	$ReCl_3(NO)(Et_2PhP)_2$	$ReBr_3(NO)(Et_2PhP)_2$	$ReCl_3(Et_2PhP)_3$
METHYL	- 1.23	- 1.27	- 1.53 - 7.53 - 8.50
METHYLENE	- 1.92	- 2.05	- 2.75 - 4.80
PHENYL	- 7.57	- 7.48	- 7.90 - 8.83 - 10.31

(a) chemical shifts as ppm downfield from TMS

(iii) ^{1}H NMR spectra :-

The paramagnetic complexes $ReX_3(NO)(Et_2PhP)_2$ (X = Cl,Br), give ^{1}H NMR spectra which are not subject to paramagnetic contact shifts[190]. However there is a very considerable broadening of the resonances, particularly in the ethyl region. The methyl and methylene resonances can be distinguished however and it is noticeable that on change of halogen from chlorine to bromine both methylene and, to a lesser extent, methyl resonances are further deshielded (Table 3.11). This deshielding is of a similar magnitude to that noted previously for square planar four coordinate complexes (Chapter 2) and for rhenium (V) oxo and nitrido complexes discussed earlier in this Chapter, and no doubt similar explanations to those given for the above cases can be applied here. Further discussion is, however, delayed until Chapter 5.

By contrast with the spectra of the rhenium (II) nitrosyl complexes, the rhenium (III) (d^4) complex, $ReCl_3(Et_2PhP)_3$, gives sharply resolved multiplets. However, these resonances are subject to considerable contact shifts. Randall and Shaw[190] have discussed the spectra of this and related compounds in some detail. The assignments of Table 3.11 have been made on the basis of the conclusions of these workers and from the observed multiplicity of the resonances.

3.2.3 Experimental

(a) Preparation of Rhenium (II) Nitrosyl Complexes :-

Trichloronitrosylbis(diethylphenylphosphine)rhenium(II),[173] $ReCl_3(NO)(Et_2PhP)_2$

(i) Trichlorotris(diethylphenylphosphine)rhenium(III)[189], $ReCl_3(Et_2PhP)_3$

$ReOCl_3(Ph_3P)_2$ (2.1gm) was suspended in benzene (50ml) and treated with Et_2PhP (2.0gm). After refluxing for 6 hours the cooled orange-brown solution was evaporated under reduced pressure to a small volume. Light petroleum (50-70) was then added. The solution deposited orange-yellow needles which were filtered, washed with light petroleum and dried in vacuo (1.35gm, 83%). m.pt. 148-152° c f. lit.[189] 150-155°. Analysis : Calculated for $C_{30}H_{45}Cl_3P_3Re$, C = 45.5%; H = 5.69%. Found : C = 45.7%; H = 5.61%.

(ii) $ReCl_3(Et_2PhP)_3$ (0.69gm) was dissolved in benzene (100ml) in a 250 ml 3-necked flask. Dinitrogen was passed over the refluxing solution and nitric oxide was bubbled through the solution for 1 hour. The orange-yellow solution changed to a purple colour which darkened as the reaction proceeded. The solvent was taken off under reduced pressure to give the crude product as a dark purple solid. This material was recrystallised from dichloromethane-methanol to yield purple rhombs (0.39 gm, 68%). m.pt. 153-157° c f. lit.[173] 155-158°. ν(NO) at 1735 cm^{-1} c f. lit.[173] 1735 cm^{-1}. Analysis : Calculated for $C_{20}H_{30}Cl_3NOP_2Re$, C = 36.6%; H = 4.58%. Found : C = 36.9%; H = 4.73%.

Tribromonitrosylbis(diethylphenylphosphine)rhenium (II), $ReBr_3(NO)(Et_2PhP)_2$

(i) Tribromotris(diethylphenylphosphine)rhenium (III)[161], $ReBr_3(Et_2PhP)_3$

The procedure was the same as for the preparation of the trichloro analogue in (1) above; however a much longer reflux

time (45 hours) was required for complete reduction. The compound was obtained as orange-brown microcrystals from benzene-ether. (85%). m.pt. 139-142° c f. lit.[161] 140-146°. Analysis : Calculated for $C_{30}H_{45}Br_3P_3Re$, C = 39.0%; H = 4.87%. Found : C = 39.1%; H = 4.94%.

The compound $ReOBr_3(Ph_3P)_2$ required as a starting material for the above reduction was prepared by the same method as for $ReOCl_3(Ph_3P)_2$ (see p. 105).except that concentrated hydrobromic acid was used in the reduction of perrhenate, and the solvent was glacial acetic acid[168]. It was also once prepared by shaking the oxoethoxo complex, $ReO(OEt)Br_2(Ph_3P)_2$, with concentrated HBr in dichloromethane[154]. Treatment of the CH_2Cl_2 extract with light petroleum (50-70) precipitated the complex as yellow rhombs in 85% yield. m.pt. 181-183°.

(ii) Tribromonitrosylbis(diethylphenylphosphine) rhenium (II), $ReBr_3(NO)(Et_2PhP)_2$

An analogous procedure to that described above for the chloro complex resulted in the formation of a deep purple solution after 45 minutes bubbling of nitric oxide through the solution. The crude complex was obtained by evaporating the benzene solution under reduced pressure. Recrystallisation from dichloromethane-methanol gave dark purple microcrystals (0.30 gm, 45%). m.pt. 159-161°. ν (NO) at 1740 cm^{-1}. Analysis : Calculated for $C_{20}H_{30}Br_3NOP_2Re$, C = 30.5%; H = 3.81%. Found : C = 30.5%; H = 3.85%.

Triiodonitrosylbis(diethylphenylphosphine)rhenium (II), $ReI_3(NO)(Et_2PhP)_2$

$ReCl_3(NO)(Et_2PhP)_2$ (0.14gm) was dissolved in acetone

and treated with sodium iodide (2.0 gm). The solution was boiled under reflux for 30 minutes and then evaporated to dryness. The crude, indigo-coloured product was extracted with dichloromethane (50 ml) and the extract washed with water (3 x 50 ml). After drying over anhydrous sodium sulphate the solution was evaporated to a small volume and treated with methanol. The indigo microcrystals of the required product were filtered off and dried in vacuo. (0.09 gm, 45%) m.pt. 133-135°. ν(NO) at 1735 cm^{-1}. Analysis : Calculated for $C_{20}H_{30}I_3NOP_2Re$, C = 25.8%; H = 3.23%. Found = C = 26.5%; H = 3.48%.

(b) Preparation of a Rhenium (I) Nitrosyl Complex :-

Dichloronitrosyltris(diethylphenylphosphine) rhenium (I), $ReCl_2(NO)(Et_2PhP)_3$

Method (i) :-

$ReCl_3(NO)(Et_2PhP)_2$ (0.30 gm) was dissolved in ethanol and treated with Et_2PhP (0.90 gm). The solution was heated to reflux and an aqueous solution of sodium sulphite was added dropwise. After 10 minutes of this treatment the solution had changed colour from purple to golden yellow, with concurrent precipitation of a white solid. The solution was cooled and extracted with dichloromethane (3 x 50 ml) and this extract washed with water (3 x 50 ml). After drying over anhydrous sodium sulphate and reducing to 20 ml residual volume attempts were made to induce crystallisation. However nothing could be obtained by ether or light petroleum treatment, and evaporation to dryness gave an oil.

It was decided to attempt to remove the free phosphine present by column chromotography. Adsorption onto alumina

(5%, 10% or 15% deactivated, Grade H) and elution with a wide variety of solvents resulted in decomposition on the column at every attempt.

However adsorption onto silica (Sorbsil) followed by thorough washing with benzene and elution with ethanol/benzene (1:10) gave a bright yellow solution which deposited yellow microcrystals upon evaporation (0.06 gm, 16%) m.pt. 216-220° c f. lit.[173] 224-226°. ν(NO) at 1665 cm^{-1} c f. lit.[173] 1660,1680 cm^{-1}. Analysis : Calculated for $C_{30}H_{45}Cl_2NOP_3Re$, C = 45.9%; H = 5.73%. Found : C = 46.6%; H = 6.07%.

Method (ii) :-

An attempted reduction of the rhenium (II) complex, $ReCl_3(NO)(Et_2PhP)_2$, with hydrazine hydrate using otherwise analogous conditions to method (i) above gave a yellow oil. However a crystalline product could not be obtained, even after recourse to all available chromatographic materials and solvents.

(c) The Reaction of Tetrachlorobis(diethylphenylphosphine) rhenium (IV) with Nitric Oxide :-

Tetrachlorobis(diethylphenylphosphine)rhenium(IV), $ReCl_4(Et_2PhP)_2$, was prepared by the oxidation of $ReCl_3(Et_2PhP)_3$, using carbon tetrachloride both as the oxidising agent and as the solvent.[189]

$ReCl_4(Et_2PhP)_2$ was dissolved in benzene and the solution was boiled under reflux. Nitric oxide was bubbled through the solution for 2 hours. Since the expected product, $ReCl_3(NO)(Et_2PhP)_2$, and the starting material are both deep purple in colour it was not possible to observe visually whether a reaction had occurred. A sample of the reaction mixture was

withdrawn and evaporated to dryness. An infra-red spectrum showed no sign of the presence of a nitrosyl stretching absorption. The remainder of the refluxing reaction solution was treated with nitric oxide for a further 4 hours. However the product recovered after evaporation was starting material, as shown by infra-red, and comparison of X-ray powder photographs.

(d) Other Attempts to Prepare Rhenium Nitrosyl Complexes :-

(i) Attempted preparation via the pentachloronitrosyl rhenium (II) anion, $[ReCl_5(NO)]^{2-}$ [169]

The starting material, $(Et_4N)_2$ $(ReCl_5(NO))$, was prepared[169] by bubbling nitric oxide through an ethanolic solution of the oxoethoxo complex, $ReO(OEt)Cl_2(Ph_3P)_2$, in the presence of tetramethylammonium chloride. The pale green compound so formed had m.pt. 270°, ν(NO) at 1720 cm^{-1} c.f. lit.[169] m.pt. 265° ν(NO) at 1720 cm^{-1}. The oxoethoxo complex was prepared by standard methods[153].

Subsequent attempts to react the pentachloronitrosyl anion with triethylphosphine or diethylphenylphosphine under a variety of conditions did not lead to identifiable products. There was no reaction at all after prolonged refluxing in absolute ethanol; in 95% ethanol/water the mixture decomposed to a brown oil.

With DMF as a solvent a golden yellow solution was obtained after heating at 100° for 16 hours. However no crystalline product could be obtained from this solution. This method was not further investigated.

(ii) The thermal decomposition of silver hexahalogenorhenate (IV) salts in the presence of nitric oxide and the reaction of the products with tertiary phosphines Silver hexahalogenorhenate (IV) salts of the form Ag_2ReX_6 (X = Cl,Br) were prepared from their potassium analogues by literature methods[191,192]. The potassium salts themselves were prepared by the methods of Rulfs and Meyer[193] (chloride) and Nyholm et al.[194] (bromide).

The thermal decomposition of Ag_2ReCl_6 in the presence of nitric oxide was carried out at 300° for 2 hours[172]. However the green product so formed was not soluble in ethanol and appeared in fact to be mostly silver chloride. Further attempts to prepare $ReCl_3(NO)$ using varying reaction times and temperatures did not lead to identifiable products.

No details were available for the preparation of $ReBr_3(NO)$ using the method of Sen et al.[171], and the same conditions as initially used for the hexachlororhenate (IV) decomposition again gave no characterisable products for the bromide. However when the conditions were changed to heating for 3 hours at 150° in a stream of nitric oxide, a crumbly red-brown material which was very soluble in ethanol was obtained. After filtering off insoluble material (mainly silver bromide) the solution was boiled under reflux with Et_2PhP (0.8 gm) for 1 hour. The wine-red solution so formed was evaporated to a small volume and treated with ether. A buff coloured solid was formed and this was filtered off and recrystallised from benzene/ether. The mother liquor was evaporated to dryness to yield a purple-red oil which could not be crystallised and was possibly a silver complex formed by reaction of excess phosphine with finely

divided silver bromide which penetrated the filter disc. The buff microcrystals obtained above had an infra-red spectrum which showed both characteristic phosphine bands and two very sharp nitrosyl stretching absorptions at 1685 and 1660 cm^{-1}. Microanalytical figures were C = 40.6%; H = 5.47%. This may be compared with those expected for $ReBr_2(NO)(Et_2PhP)_3$, C = 41.2%; H = 5.15%. The crystals had m.pt. 175-177° and the yield was 0.16 gm (20%), based on 0.79 gm Ag_2ReBr_6 starting material. The complex was diamagnetic in the solid state.

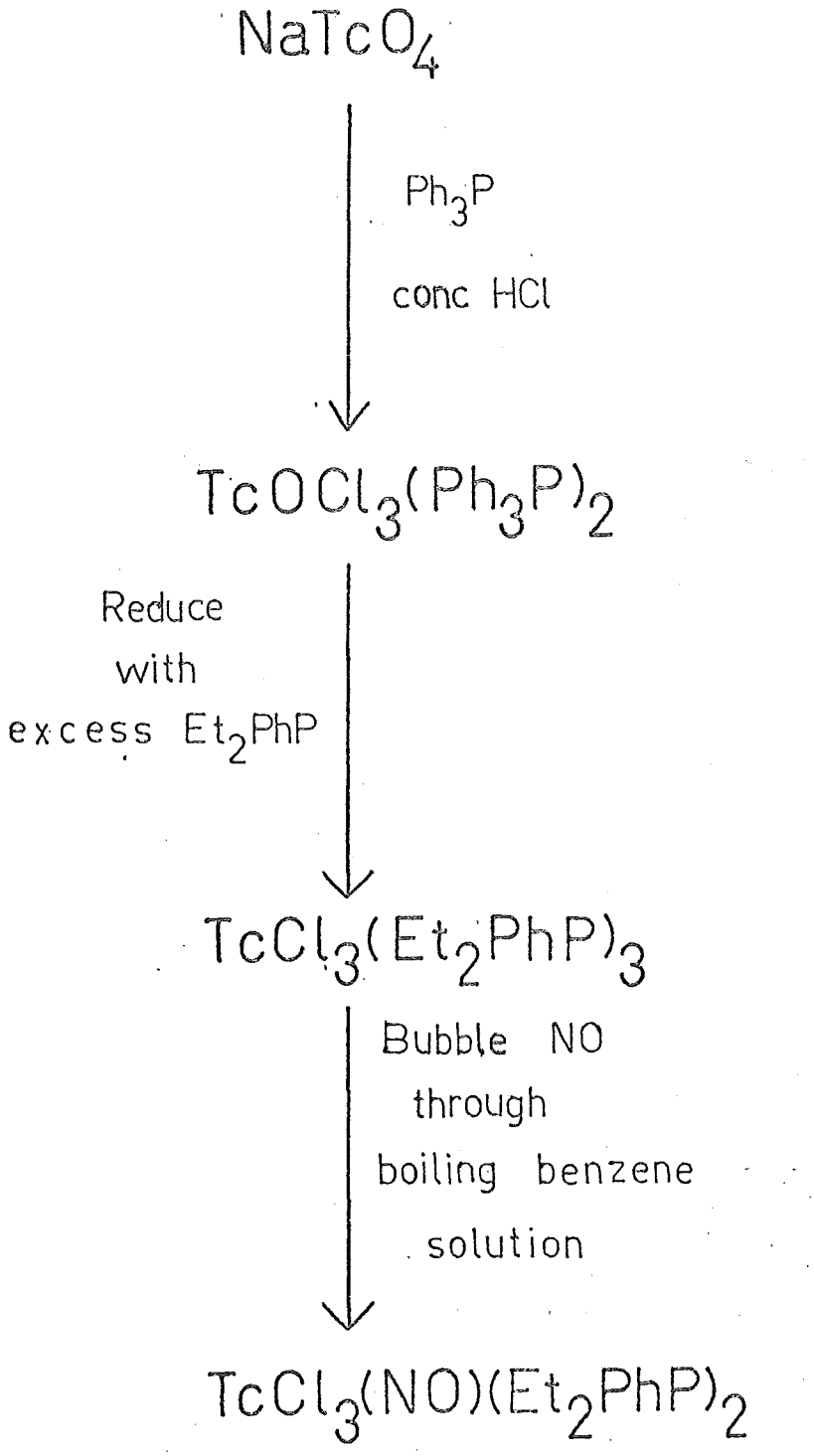
(e) Experimental details of the preliminary single crystal X-ray structural study of $ReCl_3(NO)(Et_2PhP)_2$:-

Suitable crystals of the complex were quite readily obtained. The best crystals were grown by slow evaporation of a dichloromethane solution of the complex while allowing surrounding methanol to diffuse into the solution, in a closed system. The result was a mixture of fibrous needles and chunky parallelpipeds, several of which were considered suitable for preliminary work.

Precession photographs were taken on Stoe and Supper precession cameras using Co(Kα) radiation (nickel filtered). These photographs indicated monoclinic symmetry with systematic absences $h + l = 2n + 1$ for $h\,o\,l$ and $k = 2n + 1$ for $o\,k\,o$ uniquely indicating space group $P2_{1/n}$, a special setting of $P2_{1/c}$ (C_{2h}^5, No. 14)[195]. The density, 1.74 gm cm^3, was determined by flotation in aqeous zinc bromide solution.

FIGURE 3·7

REACTION SEQUENCE FOR PREPARATION OF TECHNETIUM COMPLEXES



SECTION 3.3. ASPECTS OF THE PHOSPHINE CHEMISTRY OF TECHNETIUM

The chemistry of technetium shows many close parallels with that of rhenium but there are also some differences[196].

As an extension to the rhenium studies reported in this thesis the phosphine chemistry of technetium seemed to warrant some investigation. Little work on mono-tertiary phosphine complexes of technetium has been reported previously. Fergusson and Hickford[197] prepared $TcCl_4(Ph_3P)_2$ and related complexes by direct reaction of the tetrahalide with triphenylphosphine in refluxing ethanol. Mazzi et al.[198] have studied the reduction of ammonium pertechnetate with HX in the presence of dimethylphenylphosphine. With a pertechnetate/phosphine molar ratio of 1:5, complexes of form $TcX_4(PMe_2Ph)_2$ were obtained. When the pertechnetate/phosphine ratio was $\geqslant$ 1:15, mer-$TcX_3(PMe_2Ph)_3$ complexes were obtained.

In this work the aim was to investigate the phosphine chemistry of technetium in terms of the products obtained from reaction conditions which give well known rhenium complexes.

Thus sodium perrhenate can be reduced with hydrochloric acid in the presence of triphenylphosphine to give $ReOCl_3(Ph_3P)_2$. This compound may be further reduced by refluxing with a trialkyl or mixed alkyl/aryl phosphine to give mer-trichlorotris (phosphine)rhenium(III)complexes, and the further reaction of these complexes with nitric oxide in refluxing benzene gives the rhenium (II) nitrosyl complexes, $ReX_3(NO)(phosphine)_2$. Thus an analogous reaction sequence (Figure 3.7) was attempted for technetium.

The compounds prepared here were characterised by infra-red

spectroscopy and by their isomorphism with the rhenium analogues, as shown by X-ray powder photographs. The radioactivity of technetium and the small amounts handled prevented the determination of elemental analyses.

Discussion of experimental results :-

The reduction of sodium pertechnetate with hydrochloric acid in the presence of Ph_3P gave an emerald green crystalline compound. A sharp band in the infra-red spectrum of this complex at 1088 cm^{-1} can quite reasonably be assigned to ν(Tc-O), by analogy with the sharp band at 970 cm^{-1} for $ReOCl_3(Ph_3P)_2$ and allowance for the different masses of technetium and rhenium. Further the green technetium compound is isomorphous with $ReOCl_3(Ph_3P)_2$ as shown by X-ray powder photography. Thus this system does not give the technetium (IV) complex, unlike the results of Mazzi et al.[198] using Me_2PhP. This can be related to the relative reducing powers of the two phosphines i.e. Me_2PhP is a better reducing agent than Ph_3P.

$TcOCl_3(Ph_3P)_2$ could be reduced very rapidly with excess of Et_2PhP in benzene boiling under reflux, to give an orange crystalline material. The reaction is faster than the analogous reaction in rhenium chemistry, probably because the technetium (V) oxo complex is more soluble in benzene than the rhenium (V) oxo analogue. The orange complex was isomorphous with mer-$ReCl_3(Et_2PhP)_3$. The infra-red spectrum contained no absorption assignable to a technetium-oxygen vibration. The compound is thus formulated as $TcCl_3(Et_2PhP)_3$.

The reaction of the trichlorotris(phosphine) complex with nitric oxide in boiling benzene gave a deep green solution from which either purple or green crystals could be extracted

depending on the procedure (see p. 136). These appear to be isomers of the product which is formulated as $TcCl_3(NO)(Et_2PhP)_2$ on the grounds of isomorphism of the purple form with the rhenium analogue (the green form had a different X-ray powder photograph) and the presence of a strong band in the infra-red spectrum of both forms at 1775 cm^{-1}.

In summary then, the technetium phosphine system studied here shows a very similar chemistry to the analogous rhenium system.

Experimental details of technetium studies :-

Oxotrichlorobis(triphenylphosphine)technetium(V), $TcOCl_3(Ph_3P)_2$

Sodium pertechnetate (0.18 gm) was dissolved in hot ethanol (20 ml) in a 50 ml flask and concentrated hydrochloric acid (2 ml) was added. The solution was heated to reflux and Ph_3P (0.85 gm) in hot ethanol (10 ml) was added. An emerald green crystalline solid was immediately formed. The mixture was refluxed for 30 minutes then filtered hot and the crystals washed with ethanol. The dark emerald green material so obtained was air dried (0.56 gm, 78%). The complex was moderately soluble in benzene and slightly soluble in hot ethanol. ν(Tc-O) was assigned as 1088 cm^{-1}. As shown by X-ray powder photography the complex was isomorphous with the rhenium analogue.

Trichlorotris(diethylphenylphosphine)technetium(III), $TcCl_3(Et_2PhP)_3$

$TcOCl_3(Ph_3P)_2$ (0.4 gm) in benzene (30 ml) was boiled under reflux with Et_2PhP (0.6 gm) for 2 hours. The originally green solution had changed to an orange-brown colour at the end of this time. The solution was evaporated to 10 ml, treated

with light petroleum (50-70), and placed in an ice-salt bath for 30 minutes. The result was the deposition of bright orange needles which were filtered off, washed with ether, and air dried (0.25 gm, 58%). The complex was isomorphous with the rhenium analogue as shown by X-ray powder photographs.

Trichloronitrosylbis(diethylphenylphosphine)technetium, $TcCl_3(NO)(Et_2PhP)_2$

$TcCl_3(Et_2PhP)_3$ (0.15 gm) was dissolved in benzene (35 ml) and boiled under reflux. Nitric oxide was now bubbled through the solution and immediately a colour change occurred to give a deep sea green hue which darkened as the reaction proceeded. After 30 minutes of nitric oxide treatment the solvent was evaporated off. The dark green oily solid so formed was taken up in dichloromethane and treated with methanol. The result was the precipitation of a purple crystalline material (0.06 gm, 50%). ν(NO) at 1775 cm^{-1}. Since the complex appeared to contain some moisture (from using wet methanol) it was taken up in benzene and dried over anhydrous sodium sulphate. The result was a partial conversion to the green colour observed previously. On evaporating to dryness a mixture of purple and green solids was obtained. The green colour was extracted by washing with benzene/light petroleum (1:1). The purple material appeared to slowly revert to the green compound on standing for some weeks but the purple compound could be recovered by recrystallising from dichloromethane. The purple compound was isomorphous with the rhenium analogue as shown by X-ray powder photography. The green compound however showed a different X-ray powder diffraction pattern. It did however have a nitrosyl stretching absorption at 1775 cm^{-1} in the infra-red.

CHAPTER 4

STUDIES IN THE PHOSPHINE CHEMISTRY OF RUTHENIUM

The work described in this Chapter is concerned with some aspects of the chemistry of octahedral phosphine complexes of ruthenium (II) and (III).

SECTION 4.1 RUTHENIUM (III) COMPLEXES

4.1.1 Introduction

Trihalogenotris(phosphine) complexes of ruthenium (III) are known with chloro and bromo ligands[189,199]. The preparation of these complexes is generally by reaction of ruthenium trichloride with the phosphine in ethanol containing hydrochloric acid, and boiling the solution under reflux. The bromo complexes have been obtained by metathesis[189]. Short reaction times of the order of ten minutes lead to the required products. However, with reflux times of some hours, halogen-bridged dimeric products of form $[RuCl_3(PR_3)_2]_2$ (R = ^nPr, ^nBu) have been obtained[200].

Anionic ruthenium (III) complexes are well established. Thus complexes of form $M[RuCl_4(PR_3)_2]$ (M = Me_4N, Ph_4As; R_3 = Ph_3, Et_3, Me_2Ph) have been discussed and characterised by Stephenson[201,202].

Ruthenium (III) complexes of form RuX_3L_3 (X = Cl,Br ; L = PEt_3, Et_2PhP) have been prepared and characterised in the present work, and the complexes have been studied by electronic and low frequency infra-red spectroscopy. The infra-red spectra have been considered before by Chatt et al.[166], and interpreted

TABLE 4.1

Far infra-red spectra of some ruthenium (III) complexes [a]

BAND ASSIGNMENT	$RuCl_3(Et_2PhP)_3$	$RuBr_3(Et_2PhP)_3$	$RuCl_3(PEt_3)_3$	$RuBr_3(PEt_3)_3$
ν(M-X) a_1 (2)	332 sh,m	280 m,br	335 ms	283 m,br
ν(M-X) b_1	318 s	250 s,br	321 s	243 ms,br
ν(M-X) a_1 (1)	265 ms	167 m,br	249 m,br	165 w
ν(M-P)	250 m,sh	(b)	(b)	(b)
Other bands	382 w	327 wm	380 w	385 w
	142 w	220 w	187 wm,br	345 wm
	115 w	113 w		327 m,br
	87 wm	45 w		187 w,br

(a) frequencies in cm^{-1} (b) masked

TABLE 4.2

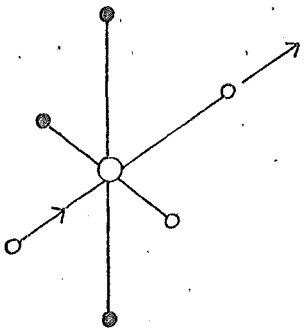
Electronic spectra of some ruthenium (III) complexes [a]

BAND ASSIGNMENT	$RuCl_3(Et_2PhP)_3$	$RuBr_3(Et_2PhP)_3$	$RuCl_3(PEt_3)_3$	$RuBr_3(PEt_3)_3$
Ligand field				
$^2T_2 \longrightarrow {}^4T_1$	860 (150)	895 (150)	843 (100)	885 (100)
$^2T_2 \longrightarrow {}^2A_2$, $^2T_1$	515 (500)	565 (700)	508 (800)	545 (850)
halogen $\longrightarrow$ metal				
$X_{nb} \longrightarrow {}_{eg}^{*}$	349 (2000)	378 sh (1400)	348 (2100)	380 (2000)
phosphorus — metal				
$P_{nb} \longrightarrow {}_{eg}^{*}$	245 (20,000)	248 (25,000)	248 (18,000)	246 (20,000)

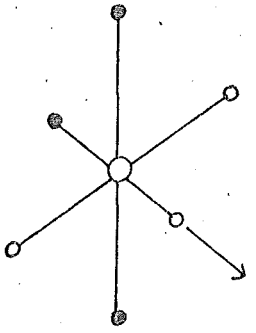
(a) wavelengths in nanometres
extinction coefficients in parentheses
sh = shoulder

FIGURE 4·1

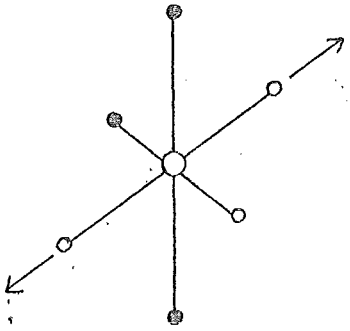
METAL-HALOGEN VIBRATIONS FOR MX_3L_3 COMPLEXES



$\nu(M-X_3)$ b_1

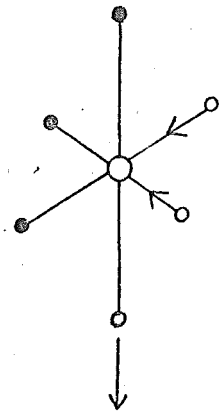


$\nu(M-X_3)$ $a_1^{(1)}$

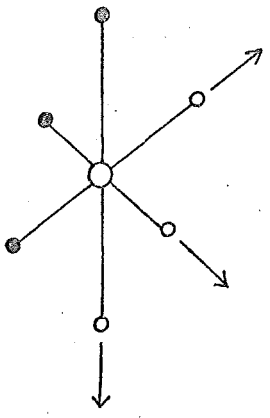


$\nu(M-X_3)$ $a_1^{(2)}$

mer isomer



$\nu(M-X_3)$ e



$\nu(M-X_3)$ a_1

fac isomer

in favour of a meridional configuration of ligands. A similar conclusion was reached from ESR studies by Hudson and Kennedy[203]. Iodo complexes have not been previously reported and attempts to prepare such compounds in the present work by metathetical reactions gave products which could not be characterised by elemental analysis and which were not further investigated.

4.1.2 Spectroscopic Studies

(a) Low-frequency infra-red spectra :-

Complexes of the form MX_3L_3 may have either a meridional or a facial arrangement of ligands. Chatt et al.[189] have shown that the mer complexes will have three and the fac complexes two possible infra-red active metal-halogen stretching modes of vibration. Fig. 4.1 shows the form which these modes will take. In a previous infra-red study[189] of RuX_3L_3 (X = Cl,Br; L = phosphine) complexes, three distinct regions of metal-halogen stretching absorption were observed, and on this basis the complexes were assigned the mer configuration.

In the present study three regions of probable metal-halogen absorption are observed in the spectra of both chloro and bromo complexes, and these have been assigned as shown in Table 4.1. The validity of the assignments is supported by comparison of the spectra of complexes differing only in phosphine, or only in halogen. The stretching vibrations of the two halogeno-ligands trans to each other should give rise to higher energy absorptions ($a_1^{(2)}$, b_1 symmetry) and the stretching vibration of the halogen trans to a phosphine ligand may be assigned to the low energy metal-halogen stretching vibration ($a_1^{(1)}$ symmetry). The observed bands are generally

broad and a number have shoulders associated with the main absorption. It is not possible in other than the complex $RuCl_3(Et_2PhP)_3$ to make adequate assignments for any of the expected ruthenium-phosphorus stretching vibrations because a strong metal-halogen vibration has been assigned in the expected region of ν(Ru-P) absorption.

In the spectrum of the complex $RuBr_3(Me_2PhP)_3$ recorded by Chatt et al.[189], ν(Ru-Br) was assigned to weak or medium intensity low energy bands (232, 224, 202 and 168 cm^{-1} respectively). These assignments are not supported for the similar complexes studied in the present work and indeed it seems very unlikely that such low energies for ruthenium-bromine stretching vibrations will be at all general for ruthenium in the trivalent oxidation state.

(b) Electronic absorption spectra :-

Ruthenium (III) has a d^5 electron configuration, for which three (or perhaps four) spin-allowed ligand field transitions are expected. The spectra obtained in the present work show two regions of absorption which may be assigned to ligand field transitions (see Table 4.2). The band at higher energy (near 500 nm) may correspond to the pair of transitions $^2T_2 \longrightarrow {}^2A_2$, $^2T_1$ which are expected to be very close in energy. Thus the extinction coefficient for this band (c. a. 700) can be rationalised as arising from two overlapping bands. The weaker band above 800 nm may be assigned to a lower energy spin-forbidden band, possibly the $^2T_2 \longrightarrow {}^4T_1$ transition.

An alternative explanation for the appearance of the 500 nm band is that it corresponds to a halogen to metal (t_{2g}) charge transfer transition, a similar situation to the more intense band

assigned to this transition in the spectra of rhenium (II) nitrosyl complexes (also d^5), discussed in Chapter 3. However, the low extinction coefficients for the band in the spectra of the ruthenium (III) complexes tend to make this explanation less likely.

There are two regions of more intense absorption in the spectra of RuX_3L_3 complexes (Table 4.2) and these probably correspond to charge transfer transitions. The band near 350 nm has an extinction coefficient of the order of 2,000, and varies with change in halogen in the manner expected for a halogen to metal charge transfer transition (see discussion, pp. 69 and 121). It is likely that the final charge transfer state involves the e_g^* metal orbitals rather than the t_{2g} orbitals, since the absorption occurs at high energy.

A band near 250 nm which is invariant with change in halogen may be assigned to a charge transfer transition between the phosphine ligand and the metal ion. The band cannot be assigned as an intra-ligand transition since only Et_2PhP shows an absorption in the free ligand state, and yet both PEt_3 and Et_2PhP complexes have the 250 nm absorption band in their spectra.

4.1.3 Experimental

The complexes of formula RuX_3L_3, where X = Cl,Br and L = Et_2PhP ; PEt_3 , were prepared by the following procedures represented here for the PEt_3 complexes.

Mer-trichlorotris(triethylphosphine)ruthenium(III), $RuCl_3(PEt_3)_3$:-

Ruthenium trichloride hydrate (1 gm) was dissolved in ethanol (25 ml) containing concentrated hydrochloric acid (5 ml),

and the solution was boiled under reflux for 10 minutes. The brown solution so formed was evaporated to a small volume and the brown microcrystals which precipitated were recrystallised from ethanol containing hydrochloric acid (1.1 gm, 58%). m.pt. 181 - 184°. Analysis : Calculated for $C_{12}H_{30}Cl_3P_3Ru$, C = 38.4%; H = 8.00%. Found : C = 38.2%; H = 7.93%.

Mer-tribromotris(triethylphosphine)ruthenium(III), $RuBr_3(PEt_3)_3$

The trichloro complex (0.4 gm) was dissolved in acetone (25 ml) containing lithium bromide (2 gm), and the mixture was boiled under reflux for 10 minutes. The solution was evaporated under reduced pressure and the solid washed well with water. The dark brown residue was recrystallised from ethanol/hydrobromic acid (0.32 gm, 65%). m.pt. 180 - 182°. Analysis : Calculated for $C_{12}H_{30}Br_3P_3Ru$, C = 31.1%; H = 6.48%. Found : C = 30.8%; H = 6.31%.

The following Et_2PhP complexes were similarly prepared

Mer-trichlorotris(diethylphenylphosphine)ruthenium(III)[189], $RuCl_3(Et_2PhP)_3$

Brown microcrystals, from ethanol/HCl, (59%). m.pt. 156 - 160°. c f. lit.[189] 159 - 162°. Analysis : Calculated for $C_{20}H_{30}Cl_3P_3Ru$, C = 51.0%; H = 6.37%. Found : C = 51.6%; H = 6.72%.

Mer-tribromotris(diethylphenylphosphine)ruthenium(III)[189], $RuBr_3(Et_2PhP)_3$

Brown-purple powder, from ethanol/HBr, (66%). m.pt. 168 - 174°. c f. lit.[189] 173-176°. Analysis : Calculated for $C_{20}H_{30}Br_3P_3Ru$, C = 42.9%; H = 5.26%. Found : C = 43.4%; H = 5.61%.

SECTION 4.2 RUTHENIUM (II) HALOGENO NITROSYL COMPLEXES CONTAINING TRIETHYLPHOSPHINE AND DIETHYLPHENYLPHOSPHINE LIGANDS

4.2.1 Introduction

The ruthenium halogeno nitrosyl complexes to be discussed in this section have the form, $RuX_3(NO)L_2$ (X = Cl,Br,I : L = PEt_3, Et_2PhP). The preparations of these complexes were first discussed in 1966 by two different groups[204,205]. Later, Townsend and Coskran[206] showed that the reaction of nitrosylruthenium trichloride with tertiary phosphines, L, produced a number of products, among which were two isomers of $RuCl_3(NO)L_2$ in proportions dependent upon the nature of L, and on the reaction conditions employed. In general, the isomer with the phosphine ligands trans to each other was the major product. In the present work the only product isolated from the treatment of $RuCl_3(NO)$ with PEt_3 or Et_2PhP has been the trans isomer, as shown by ^1H NMR spectroscopy (see later). The bromo and iodo complexes were prepared from the chloro analogues by metathetical reaction with either lithium bromide or sodium iodide.

The high value of the nitrosyl stretching frequency in the infra-red spectra of these complexes[204-206] indicates that the nitric oxide ligand is probably coordinated as NO^+. It may be recalled from previous discussion (p. 116) that the frequency of the $\nu(NO)$ vibration is not necessarily diagnostic of the type of coordination of the ligand (i.e. either NO^+ or NO^-), although in this case the value in the region of 1850 cm^{-1} is strongly suggestive of the presence of NO^+ since the general range for NO^- stretching absorption is considered to be below 1700 cm^{-1}. The probability of the nitric oxide ligand being coordinated as NO^+

TABLE 4.3

Far Infra-Red Spectra : Assignments for $RuX_3(NO)L_2$ (L=PEt_3, Et_2PhP) Complexes

BAND ASSIGNMENT	$RuCl_3(NO)(Et_2PhP)_2$	$RuBr_3(NO)(Et_2PhP)_2$	$RuI_3(NO)(Et_2PhP)_2$	$RuCl_3(NO)(PEt_3)_2$	$RuBr_3(NO)(PEt_3)_2$	$RuI_3(NO)(PEt_3)_2$
ν(Ru-X) trans to nitrosyl	339 s			337s		
	320 s	259ms	227wm	322ms	260s	219m
ν(Ru-X) trans to X	290m	223m	157m	289m	228m	161m
ν(Ru-P)	255m	249s	(b)	241ms	(b)	252m
δ(MPC)	212ms	204ms	202ms	191m	180ms	177wm
		317ms	316ms	385m	380m	385w
		300wm	302ms		338m	380w
Other	168sh,m	276m			318m	349wm
bands	160m	181w,br	187w	165m	167m	177w
	125w,br	154ms		157m,sh	145w	143w
	75w	123w		76wm	70wm	102w
		114w				82w
		67w,br				

(a) frequencies in cm^{-1} (b) masked

therefore leads to the formulation of the complexes as those of ruthenium (II). This is supported by the observed diamagnetism of the complexes, which can be expected for a d^6 second-row transition metal ion in octahedral coordination. Also the determination[184] of the single crystal X-ray structure of the complex $RuCl_3(NO)(MePh_2P)_2$ has shown that the Ru-N-O bond angle is 176° and hence the nitrosyl is coordinated in a linear fashion. This is expected for NO^+ (see p. 113 .) and thus the above formulation is further confirmed.

The complexes have been studied in the present work by ^1H, ^{13}C and ^{31}P NMR, far infra-red and electronic absorption spectroscopy. Some metal-ligand infra-red stretching frequencies have been reported previously[206] and the ^1H NMR spectra of a number of the complexes have been briefly discussed[206]. The preparative details for the complexes are given in Section 4.4 together with details for the analogous preparation of complexes with para-substituted phosphine ligands.

4.2.2 Results of spectroscopic studies

(a) Far infra-red spectra :-

The $RuX_3(NO)L_2$ (L = PEt_3, Et_2PhP) complexes have infra-red spectra where the metal-halogen stretching frequencies can be readily assigned, both on the basis of the relatively strong intensity of these absorptions and by comparison of complexes differing only in halogeno-ligand. In this way the assignments of Table 4.3 have been made.

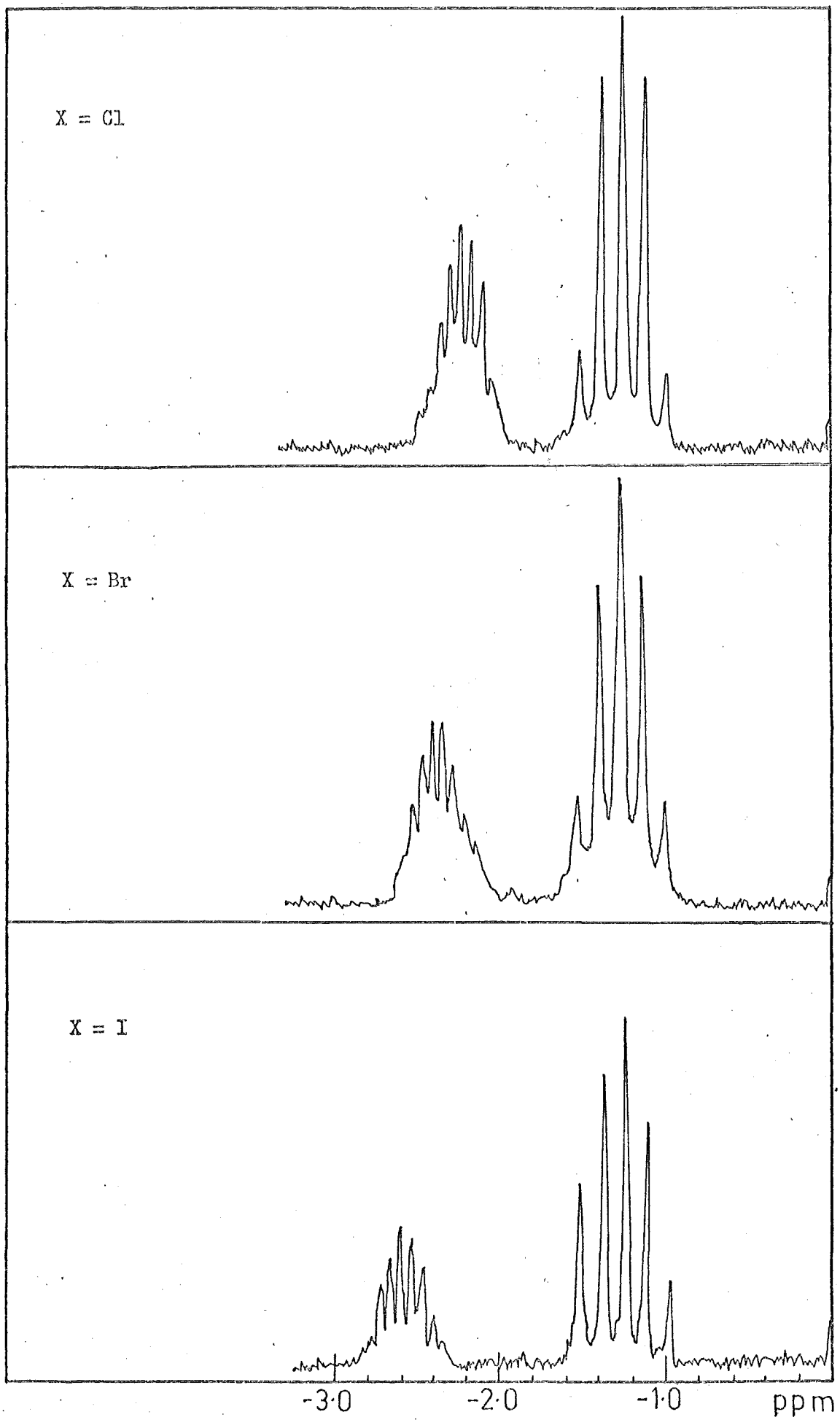
There should be three regions of absorption corresponding to metal-halogen vibrations in these complexes with a trans arrangement of phosphine ligands (and a meridional arrangement of halogens). In general, however, only two bands can be assigned

to metal-halogen stretching vibrations, except in the chloro complexes. In the previous work[206] the higher energy band was assigned to the stretching vibration of the trans halogens and the lower energy band to the stretching vibration of the halogen trans to the nitrosyl ligand. This is reasonable on the basis of the expected strong trans influence of the nitrosyl ligand. This influence may be expected to weaken the ruthenium-halogen bond hence leading to a lower infra-red stretching frequency than for the less-affected Ru-Cl bonds trans to each other. However, these assignments[206] were made before the publication of the single crystal X-ray structure determination[184] of the complex, $RuCl_3(NO)(MePh_2P)_2$ for which relevant structural data have been given elsewhere in this thesis (Table 3.8). In this complex the length of the Ru-Cl bond trans to the nitrosyl is, in fact shorter (235.7 pm) than the Ru-Cl bond lengths of the trans Cl-Ru-Cl system (240.5, 239.1 pm). A similar relative situation is found (see also Table 3.8) for the isomorphous rhenium complex, $ReCl_3(NO)(MePh_2P)_2$. This shorter bond in the position trans to a ligand considered to have a strong trans influence is a rather unexpected result, but may in fact be quite general since in the $[RuCl_5(NO)]^{2-}$ anion the Ru-Cl bond trans to nitrosyl is again marginally shorter than the other ruthenium chlorine bonds[210,211]. Presumably the back bonding of metal charge into the nitrosyl π^* orbitals in these complexes may act to enhance the σ bonding of the trans chloro ligands.

On the basis of the shorter bond length for the Ru-Cl bond trans to NO in $RuX_3(NO)L_2$ complexes, then this bond can be considered to have a higher stretching force constant than the mutually trans Ru-Cl bonds and hence one may expect a higher stretching frequency for the Ru-Cl (trans to NO) bond. In this

FIGURE 4·2

^1H NMR SPECTRA : $RuX_3(NO)(PEt_3)_2$ COMPLEXES



way the assignments of metal-halogen stretching frequencies have been made (Table 4.3).

The infra-red spectra[206] of $RuX_3(NO)(MePh_2P)_2$ complexes have metal-halogen absorptions at 339, 320 and 290 cm^{-1} (chloro complex), and around 260 cm^{-1} (bromo complex). In the present work with complexes of PEt_3 and Et_2PhP, similar assignments have been made.

The ruthenium-phosphorus stretching absorptions cannot always be adequately assigned because of the presence of intense metal-halogen bands in the expected region of ν(Ru-P), particularly for the bromo complexes. It is of interest that the metal-phosphorus stretching frequencies for these ruthenium (II) complexes are very similar to the palladium (II)-phosphorus stretching frequencies previously discussed in Chapter 2.

A band near 200 cm^{-1} in the Et_2PhP complexes and 180 cm^{-1} in the PEt_3 complexes is in general of medium intensity. It is likely that the absorption corresponds to the metal-phosphorus carbon bending mode, δ(MPC). This assignment is made on the basis of its similar position and intensity to the band assigned to δ(MPC) in the square planar complexes (Chapter 2).

Other bands in these spectra are generally of weak intensity and specific assignments have not been attempted. Absorptions in the 400 - 350 cm^{-1} region occur in all the spectra and are probably due to ligand deformations.

(b) ^{1}H NMR spectra :-

The spectra obtained for these d^6 diamagnetic complexes are notable for their excellent resolution (Fig. 4.2).

That the complexes studied here have a trans arrangement of phosphine ligands is obvious from the multiplet patterns

TABLE 4.4

^{1}H NMR Spectra of $RuX_3(NO)L_2$ (L = PEt_3, Et_2PhP) Complexes [a]

ASSIGNMENT	$RuCl_3(NO)(Et_2PhP)_2$	$RuBr_3(NO)(Et_2PhP)_2$	$RuI_3(NO)(Et_2PhP)_3$	$RuCl_3(NO)(PEt_3)_2$	$RuBr_3(NO)(PEt_3)_2$	$RuI_3(NO)(PEt_3)_2$
methyl	- 1.25	- 1.23	- 1.27	- 1.27	- 1.27	- 1.27
methylene	- 2.70	- 2.87	- 3.15	- 2.22	- 2.34	- 2.62
phenyl meta and para	- 7.44	- 7.41	- 7.34			
phenyl ortho	- 7.59	- 7.65	- 7.66			

(a) chemical shifts in ppm downfield from TMS

evident in the spectra, in which strong virtual coupling of the trans phosphorus atoms gives rise to the familiar 1:4:6:4:1 quintet for the methyl multiplets and an approximate 1:4:7:7:4:1 sextet for the methylene multiplets. The way in which these multiplets will arise has been discussed for the analogous intensity ratios found for trans square planar complexes (Chapter 2). The relevant coupling constants for the phosphorus-proton coupling interaction are 16Hz for $^{2}J(^{31}P-^{1}H)$(methyl), and 7Hz for $^{1}J(^{31}P-^{1}H)$(methylene). There is no measurable variation in these values with either change in halogeno-ligand or change in phosphine.

For the complex $RuI_3(NO)(Et_2PhP)_2$ there is some evidence for a further small splitting (c.a. 1Hz) in the methyl resonance multiplet. It seems reasonable to attribute this to a lack of complete free rotation about the carbon-carbon bond, as this complex will have the greatest steric interactions.

In Et_2PhP complexes the phenyl region shows evidence of two distinct proton environments in the ratio 2:3. The furtherest deshielded of this pair of resonances is assigned to the ortho protons and the larger area multiplet to the meta and para protons.

With change in halogen in the order Cl,Br,I the methylene multiplet is increasingly deshielded (Table 4.4). This deshielding has been noted before for the square planar complexes (Chapter 2) and rhenium complexes (Chapter 3). The methyl resonance is relatively constant with change in halogen. The ortho proton resonance of the Et_2PhP complexes also moves downfield with change in halogen, while the main phenyl proton resonance is essentially constant. Several authors have noted a similar effect in the ^{1}H NMR spectra of ruthenium (II) carbonyl[117] and nitrosyl

TABLE 4.5

^{13}C NMR Spectra of $RuX_3(NO)L_2$ (L = PEt_3, Et_2PhP) Complexes [a]

ASSIGNMENT	$RuCl_3(NO)(Et_2PhP)_2$	$RuBr_3(NO)(Et_2PhP)_2$	$RuI_3(NO)(Et_2PhP)_2$	$RuCl_3(NO)(PEt_3)_2$
methyl	- 7.4s	- 8.0s	- 9.17s	- 7.6s
methylene	-12.6t (30)	-14.93t (29.4)	-20.40t (32.8)	-14.2t (28)
C_1	-	-151.85s [b]	-	
C_{ortho}	-130.3t (8)	-130.26s	-130.28s	
C_{meta}	-128.7t (8)	-128.52t (9.2)	-128.32t (7.2)	
C_{para}	-130.3s	-130.18s	-130.07s	

(a) Chemical shifts in ppm relative to TMS as zero coupling constants (Hz) in parenthesis
s, singlet ; t, triplet

(b) observed on addition of $Cr(acac)_3$

complexes[206] and have tentatively ascribed it to $M_{d\pi} \longrightarrow X_{d\pi}$ bonding, as has been discussed previously in this thesis (Chapter 2). It is of some interest that the overall deshielding is larger in these ruthenium (II) nitrosyl complexes than is found for the square planar complexes. This can be related to the presence of the nitrosyl in the ruthenium compounds. Back bonding of metal charge into empty NO antibonding orbitals can be considered to occur and this is probably a major factor in the greater deshielding of the methylene protons observed here. Thus the presence in these complexes of a strong π -acceptor ligand such as nitric oxide has a considerable effect on charge distributions within the molecules.

(c) ^{13}C NMR spectra :-

The ^{13}C NMR spectra of the three complexes $RuX_3(NO)(Et_2PhP)_2$ (X = Cl,Br,I) and of $RuCl_3(NO)(PEt_3)_2$ have been obtained here. The methyl carbon resonances are singlets in all cases and no coupling with the phosphorus nuclei is observed. The methylene multiplets are well-defined 1:2:1 triplets, as expected for a trans arrangement of phosphine ligands.

The phenyl carbon multiplets are of some interest. The addition of tris(acetylacetonato)chromium(III)has little effect on the spectra, except for $RuBr_3(NO)(Et_2PhP)_2$ where a singlet resonance appears at 151.85 ppm. This may be assigned to the C_1 carbon atom. The complex $RuCl_3(NO)(Et_2PhP)_2$ shows a triplet for both the ortho and meta carbons (Table 4.5) and a singlet for the para carbon. This situation is thus analogous to that observed for square planar complexes (Chapter 2) and can be explained on the basis of the virtual coupling of the trans phosphorus nuclei. However, for bromo and iodo complexes with Et_2PhP as ligand only a singlet is observable for the ortho

carbon resonance, while a triplet is observed for the meta carbon. The good resolution of these spectra and the inability to distinguish any structure on the ortho carbon resonance at the maximum spectral amplitude imples that if any coupling interaction exists it is less than the resolving power of the instrument. It may be that the coupling interaction is transmitted via the interaction of the π system of the phenyl ring with the empty d orbitals of phosphorus, since it is hard to justify the general appearance of ortho and meta carbon-phosphorus coupling in spectra of other Et_2PhP complexes, when the methyl carbon of the ethyl groups (for which no π-bonding is expected) in these complexes is not subject to such coupling. However, why only $RuCl_3(NO)(Et_2PhP)_2$ shows an ortho carbon interaction with ^{31}P here and why the bromo and iodo complexes do not, is not clear.

Both methyl and methylene carbon atoms are deshielded when the halogen is changed in the order Cl,Br,I (Table 4.5). Similar explanations can be advanced as previously given in some detail in Chapter 2.

(d) ^{31}P NMR spectra :-

Introduction

The ^{31}P NMR spectra of a number of ruthenium (II) halogeno-phosphine nitrosyl complexes have been recorded in this work. The number of complexes which could be studied by this technique was limited by the solubility of the complexes in chloroform solution and the amount of sample available since, as already discussed in Chapter 2, the phosphorus-31 nucleus has only 6.63% of the NMR sensitivity of the proton, and hence a large amount of sample is required. Also, there are only two

TABLE 4.6

^{31}P NMR spectra of ruthenium (II) halogeno-phosphine nitrosyl complexes

Compound	Chemical shift (a)
PEt_3	+ 20.1 (b)
Et_2PhP	+ 17.6 (b)
$RuCl_3(NO)(Et_2PhP)_2$	- 12.5
$RuBr_3(NO)(Et_2PhP)_2$	- 4.0
$RuI_3(NO)(Et_2PhP)_2$	+ 10.0
$RuCl_3(NO)(PEt_3)_2$	- 16.0

(a) chemical shifts in ppm downfield from 85% H_3PO_4

(b) data from reference 130

^{31}P nuclei per molecule in these ruthenium (II) complexes. Table 4.6 contains the chemical shifts recorded for ^{31}P nuclei in the complexes studied in this work.

Discussion:

The ^{31}P NMR spectra of ruthenium (II) bis(phosphine) complexes show a single peak for all the complexes studied. This implies that the phosphine environments are identical in the compounds.

The free ligand ^{31}P NMR spectra for PEt_3 and Et_2PhP are also given in Table 4.6. Upon coordination there is a large downfield shift of the ^{31}P resonance for each ligand. This is to be expected on the basis of the lone pair donation from the phosphine ligand in forming a coordinate σ bond with ruthenium (II). On change of halogeno-ligand in the order Cl,Br,I there is now a consistent upfield shift for the ^{31}P resonance. This is the opposite trend to that observed in the ^{1}H and ^{13}C NMR spectra with change in halogen in the above order. However, the observed trend may be explained in a similar manner to the explanation already given for the situation in ^{1}H and ^{13}C spectra i.e. as being due to a draw-off of charge from the organic groups on the phosphine ligands towards the metal ion as the halogen changes in the order Cl,Br,I. This will lead to an increase in σ electron density in the metal-phosphorus bond, and therefore to some extent about the phosphorus atom. This would result in a shielding effect, as is observed. Thus the variations in chemical shifts for ^{1}H, ^{13}C and ^{31}P NMR spectra are all explicable in terms of charge draw-off of the type noted above.

TABLE 4.7

Electronic Absorption Spectra of $RuX_3(NO)L_2$ (L=PEt_3,Et_2PhP) complexes [a]

Compound	halogen ⟶ metal $X_{nb.} \longrightarrow M$ eg *	intra - ligand	metal-nitrosyl (see text)
$RuCl_3(NO)(Et_2PhP)_2$	320 (9,000)	285 (15,000)	
$RuBr_3(NO)(Et_2PhP)_2$	342 (6,000)	295 (15,000)	
$RuI_3(NO)(Et_2PhP)_2$	360 (1,500)		258 (5,500)
$RuCl_3(NO)(PEt_3)_2$	311 (3,000)		268(14,000)
$RuBr_3(NO)(PEt_3)_2$	343 (1,000)		279 (2,000)
$RuI_3(NO)(PEt_3)_2$	385 (1,000) 314 (1,300)		260 (5,000)

(a) wavelengths in nanometres
extinction coefficients in parentheses

(e) Electronic absorption spectra :-

The ligand field bands for these complexes were not observable due to interference of an intense charge transfer band in the expected region. However, two regions of charge transfer absorption can be observed in the ultra-violet region of the spectra. The observed bands, extinction coefficients and assignments are given in Table 4.7.

The band in the 300-400 nm region which shifts to lower energy on change in halogen in the order Cl,Br,I can be readily assigned to a halogen to metal charge transfer transition. The extinction coefficient for this band is of the order of 5,000 - 10,000 for Et_2PhP complexes but is somewhat lower for PEt_3 complexes.

The other band assignable to charge transfer absorption is a little anomolous. The variation of this band with change in halogeno-ligand is neither large enough for it to be assigned to a second halogen to metal charge transfer transition nor constant enough to allow it to be a phosphine-metal charge transfer transition. Results for complexes of para-substituted phosphine ligands suggest that the phosphine-metal charge transfer band in complexes of the unsubstituted Et_2PhP ligand (and therefore probably of PEt_3 also) will be at higher energy (see later discussion, p. 159).

The difficulty here is in fact one of solubility. The complexes are only moderately soluble in chloroform and poorly soluble in methanol or ethanol, or indeed any common solvent which is itself devoid of absorption in the higher energy ultra-violet region (below 240 nm). Thus it was not possible to investigate the spectra below 240 nm since this is the limit of

transparency[207] for chloroform.

The bands at 285 and 295 nm for $RuCl_3(NO)(Et_2PhP)_2$ and its bromo analogue respectively may be assigned to an intra-ligand transition of the Et_2PhP ligand, since this ligand has an absorption at 290 nm in the free state. However, no similar band is observed for the iodo complex with this ligand (Table 4.7). The ligand, PEt_3, has no intra ligand absorptions in the region studied and hence the band varying from 260 to 280 nm in complexes of this ligand cannot be assigned to such a transition. A possible explanation is that, at least for the three PEt_3 complexes and for $RuI_3(NO)(Et_2PhP)_2$, the high energy band corresponds to a charge transfer transition between the metal ion and the nitrosyl ligand, possibly of the type metal $\rightarrow$ nitrosyl (π^*).

SECTION 4.3 PARA-SUBSTITUTED DIETHYLPHENYLPHOSPHINE COMPLEXES OF RUTHENIUM (II)

4.3.1 Introduction

This section describes spectroscopic studies on complexes of the form $RuX_3(NO)(L_2$ (where X = Cl,Br,I and L = (p-QPh)Et_2P, Q = Me_2N, MeO, Cl). The analogous $RuX_3(NO)(Et_2PhP)_2$ complexes discussed in Section 4.2 can be considered as part of this study as well, with the para-substituent in this case being p-H. The compounds were prepared by the general method of reacting $RuCl_3(NO)$ with the required phosphine ligand in 2-methoxyethanol. The bromo and iodo complexes were prepared by metathesis. The specific reaction procedures are detailed in Section 4.4.

The para-substituents on the phenyl ring of the phenyldiethylphosphine ligands provide a reasonable range of electronic effects as measured by the Taft σ_p substituent constants.

That the use of the σp constants is valid here has been shown by Stepanov et al.[208], who correlated the pK_a s for some para-substituted phenyldiethylphosphines against σp. A good correlation proved possible. The substituents have values of σp ranging from -0.83 ($p\text{-}Me_2N$) ; -0.27(p-MeO) ; 0.00(p-H) and +0.23(p-Cl).

The pK_a correlation mentioned above suggests that the coordinating power of the ligand will be affected by the nature of the para-substituent on the phenyl ring. Thus spectroscopic parameters may be modified in a manner which can be related back to the electronic effect of the substituent. Steric effects of substitients may be expected to be minor, both on account of the relatively remote position of substitution and the small size of the substituent groups.

No extensive studies of this type on metal phosphine complexes appear to have been made before, although Coates et al.[90] have shown that the electronic effect of the Me_2N group (mesomeric electron-donating) in the ligand para-dimethylaminophenyldiethylphosphine is sufficient to make zinc complexes of this ligand more stable than analogous complexes of the unsubstituted Et_2PhP ligand.

The complexes have been studied by low and high frequency infra-red spectroscopy ; ^1H, ^{13}C and ^{31}P NMR ; and electronic absorption spectroscopy. Only <u>trans</u> isomers have been obtained for these complexes, as shown by ^1H NMR studies (see later discussion). The complex $RuI_3(NO)((p\text{-}ClPh)Et_2P)_2$ could not be characterised by elemental analyses, although the infra-red spectrum showed a nitrosyl stretching absorption in the expected region as well as characteristic phosphine bands. The preparation of the phosphine ligands is discussed in Chapter 6.

TABLE 4.8

Nitrosyl stretching frequencies for para-substituted phenyldiethylphosphine complexes (cm^{-1})

Ligand	chloro	bromo	iodo
Et_2PhP	1856	1852	1848
(p-Cl Ph)Et_2P	1849	1847	1840(br)
(p-Me OPh)Et_2P	1836	1858(a) 1832	1850(a) 1842
(p-Me_2NPh)Et_2P	1839(a) 1829	1835 (a) 1812	 1822

(a) higher frequency component is the more intense

4.3.2 Results and discussion of spectroscopic studies

(a) High frequency infra-red spectra :-

The nitrosyl stretching frequency occurs in the 1800-1860 cm^{-1} region for these complexes, and the values are listed in Table 4.8. The bands observed are split in several cases, presumably due to crystal effects, making any comparisons of doubtful validity. It can be generally noted, however, that although there are changes in the value of ν(NO) between the various phosphine ligands with the same halogen these changes cannot be correlated with the substituent constants. The nitrosyl stretching frequency may however be rather unsuitable for this type of correlation since it is not really clear what part solid state effects may play in the observed nitrosyl stretching absorptions. X-ray powder photographs show that, at least for chloro and bromo complexes however, the compounds all appear to have the same structure.

The values of ν(NO) for the p-chloro substituted ligand should, if a correlation were to be observed, be at rather higher energy than is observed, in fact higher than the absorption for the Et_2PhP (p-H) complexes. Apart from the (p-ClPh)Et_2P complexes however, the general trend to lower frequency for ν(NO) with p-MeO and p-Me_2N substituents as compared with p-H (Et_2PhP complexes) can be rationalised in terms of the mesomeric release of charge to the metal ion from the +R substituents. Delocalization into the antibonding nitrosyl π^* orbitals and hence a lowering of the stretching frequency could then be expected. In view of the poor correlation discussed above however, ascribing the observed lower frequencies for p-MeO and p-Me_2N complexes to mesomeric electron release alone can be no more than tentative.

TABLE 4.9

Far Infra-Red Spectra [a] : $RuX_3(NO)L_2$ complexes where L = $(p\text{-}QPh)Et_2P$; Q = Me_2N,MeO,H,Cl

BAND ASSIGNMENT	p-Me_2N	p-MeO	p-H	p-Cl	p-Me_2N	p-MeO	p-H	p-Cl	p-Me_2N	p-MeO	p-H
ν(Ru-X) trans to nitrosyl	325s	323m	339s 320s	319m	269m	265m	259ms	253	227wm	226wm	227wm
ν(Ru-X) trans to X	282m	295m	290m	274wm	230m	231ms	223m	223m,br	167w	155wm	157m
ν(Ru-P)	255wm	256m	255m	256m	261m	(b)	249s	(b)	262wm	252m	(c)
Other bands	287w	387m		385m	380m	380m		285w	390w	385m	
	208wmbr	341m		366m	355wm	348m		360w	380w	345w	
	160w	326m	(d)	343m	217w	322w		323w	275m	110w	(d)
	125w	175wm		191wm	197w	301w		205w	185w	70w	
		155w		135w	177w	145w		183w,br	137w		
		125w			158w	82w		163w	102w		
		90w			136w			73w	70w		
					82w						

(a) frequencies in cm^{-1} (b) masked (c) no absorption assignable

(d) other bands given previously in Table 4.3

(b) Low frequency infra-red spectra :-

The low frequency infra-red spectra of the complexes have been recorded in the 400-40 cm^{-1} region and are represented in Table 4.9. The spectra have been assigned in the same way as noted previously for the Et_2PhP and PEt_3 complexes discussed in Section 4.2.

The variation of analogous absorptions in complexes differing only in para-substituent on the phosphine ligand is not consistent. For the bromo complexes the ν(Ru-Br) stretching frequency for the bromine *trans* to the nitrosyl ligand is found at 269 cm^{-1} for p-Me_2N and 253 cm^{-1} for p-Cl, with the values for p-MeO and p-H(Et_2PhP) lying in between these extremes (Table 4.9). The error in measurement is $\pm$ 2 cm^{-1} so the trend is significant, and is in the same order as the trend in Taft σ_p parameters for the para-substituents. The chloro complexes show a similar trend but over a much smaller range. However, the ν(Ru-X) *trans* to halogen stretching frequency does not follow any such trend, and in fact this stretching vibration occurs at highest frequency for p-MeO.

As shown by the previous discussion of trends in nitrosyl stretching frequencies with change in para-substituent, the electronic effects of the substituents have an influence on ν(NO). This suggests that the ruthenium-chlorine bond *trans* to the nitrosyl ligand might also be affected to some extent and, as noted above, a correlation of ν(Ru-Cl) with σ_p has been observed. This is thus confirmatory evidence for the assignment of the higher-lying Ru-Cl stretching frequency to the bond *trans* to the nitrosyl ligand, as discussed in Section 4.2 (p. 144) on the basis of ruthenium-chlorine bond lengths.

TABLE 4.10

^1H NMR spectra [a] : $RuX_3(NO)L_2$ complexes where

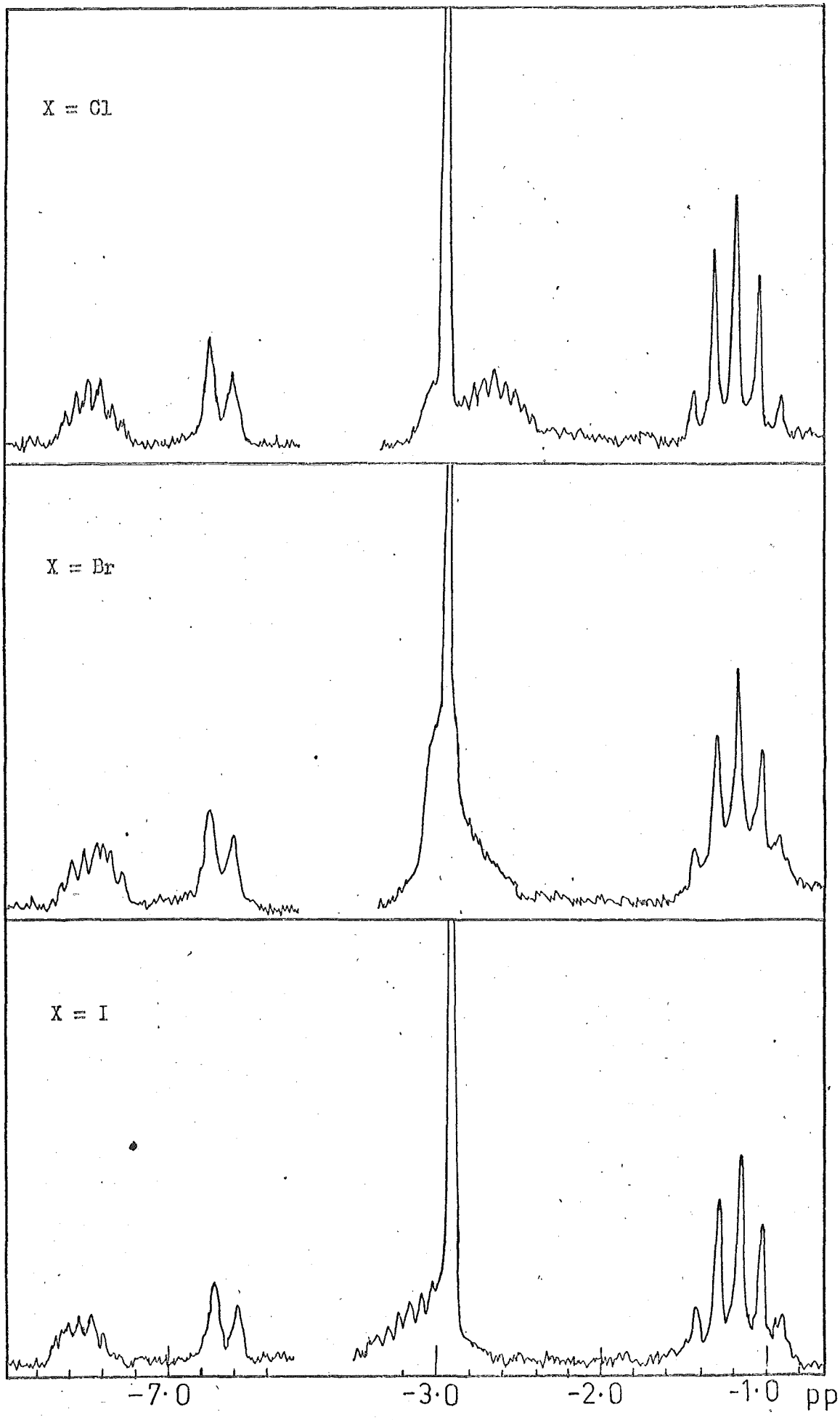
L = $(p\text{-}QPh)Et_2P$; Q = MeO, Me_2N, Cl, H

Q	Compound X	methyl	methylene	Q protons	Phenyl meta	Phenyl ortho
$p\text{-}Me_2N$	Cl	-1.17	-2.63	-2.94	-6.67	-7.45
	Br	-1.17	-2.86	-2.92	-6.65	-7.46
	I	-1.18	-3.12	-2.92	-6.64	-7.51
p-MeO	Cl	-1.18	-2.67	-3.78	-6.92	-7.54
	Br	-1.20	-2.85	-3.77	-6.92	-7.60
	I	-1.21	-3.20	-3.83	-6.92	-7.65
p-Cl	Cl	-1.23	-2.65		-7.50	
	Br	-1.17	-2.83		-7.41	
p-H	Cl	-1.25	-2.70		-7.44	-7.59
	Br	-1.23	-2.87		-7.41	-7.65
	I	-1.27	-3.15		-7.34	-7.66

(a) chemical shifts in ppm downfield from TMS

FIGURE 4·3

^1H NMR SPECTRA: $RuX_3(NO)L_2$ COMPLEXES WHERE L= $(p\text{-}Me_2NPh)Et_2P$



(c) ^{1}H NMR spectra :-

The ^{1}H NMR spectra obtained for these complexes are presented in Table 4.10. The way in which the various multiplicities arise for the several resonance regions has been considered elsewhere in this thesis (Chapter 2). Briefly it can be noted that the virtual coupling of phosphorus nuclei observed here indicates that the phosphine ligands are trans to each other. Thus the methyl multiplets are quintets with a value of $^2J(^{31}P-^1H)$ of 16 Hz in all spectra. Similarly, an approximate sextet for the methylene multiplets with $^1J(^{31}P-^1H)$ = 7Hz , occurs in all cases although the resolution of this is not always good. In the dimethylamino complexes the resonance due to the Me_2N group is a sharp singlet and it rather obscures the ethyl group methylene proton resonance multiplet (Fig. 4.3).

The phenyl regions are of considerable interest in these complexes. There are two types of protons with the presence of a para-substituent on the ligands and these resonate at quite widely different field positions for p-MeO and p-Me_2N as para-substituents. The phenyl region for the p-Cl substituted ligand complexes is not affected in this manner. The spectra of the p-Me_2N substituted complexes are shown in Fig. 4.3. For p-Me_2N and p-MeO substitution the more shielded doublet in the phenyl region can be assigned to the protons meta to the phosphorus atom and the approximate quintet further downfield to the protons ortho to the phosphorus. This follows quite naturally from a consideration of the mesomeric effects of the p-MeO and p-Me_2N groups. This has been alluded to in Chapter 2 where the complexes of (p-MeOPh)Et_2P with palladium (II) were discussed. Mesomeric electron release will result in a residual negative charge at the positions meta to the carbon-phosphorus bond (or ortho to the

TABLE 4.11

^{13}C NMR Spectra : $RuX_3(NO)L_2$ complexes where L is a para-substituted phenyldiethylphosphine ligand [a]

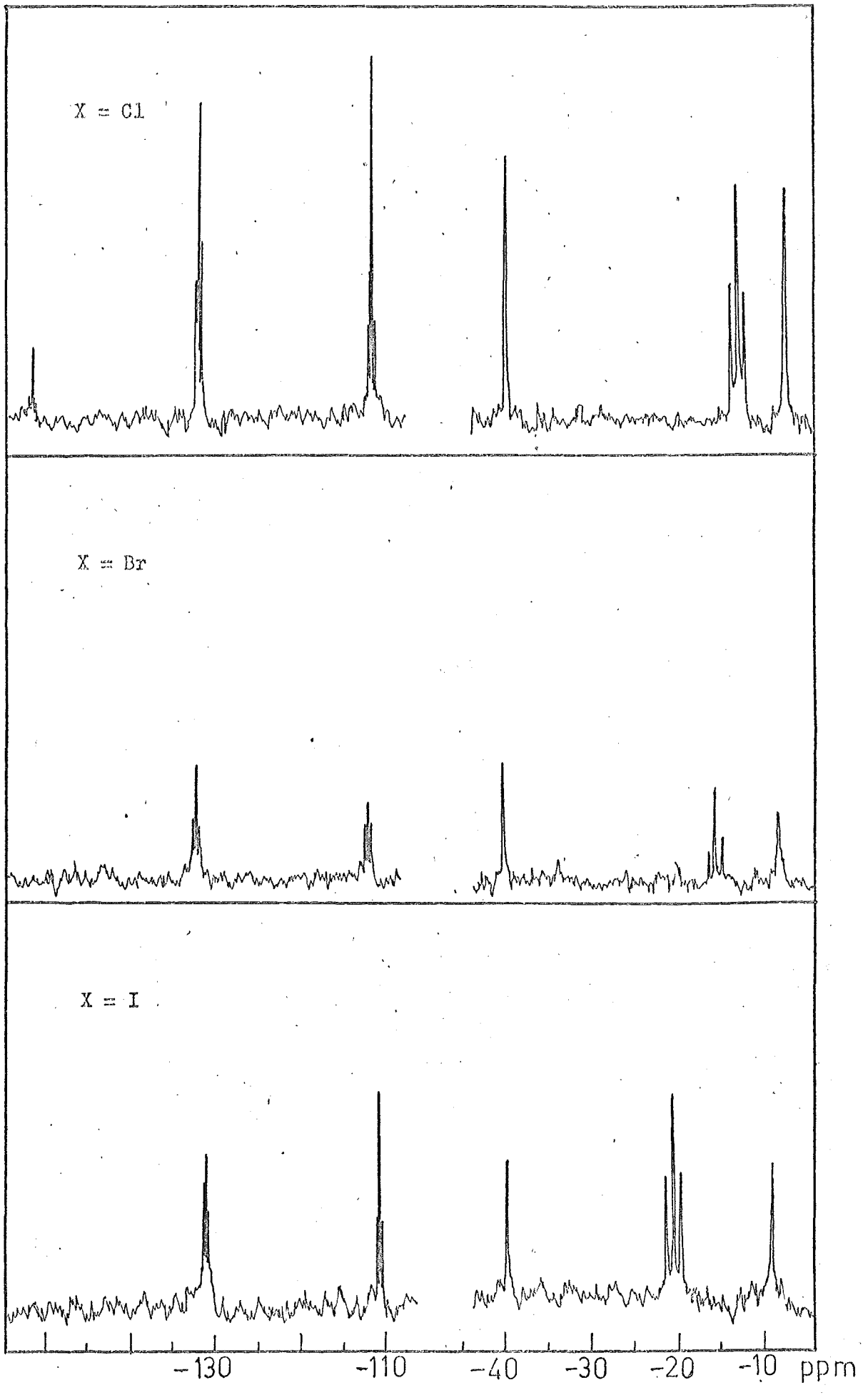
Compound	methyl	methylene	p-Me_2N	C_1	C_{meta}	C_{ortho}	C_{para}
$RuCl_3(NO)((p\text{-}Me_2NPh)Et_2P)_2$	-7.41s	-12.97t(29.2)	-39.85s	-151.32d(6.2) [b]	-111.62t(9.6)	-131.54t(9.2)	
$RuBr_3(NO)((p\text{-}Me_2NPh)Et_2P)_2$	-7.91s	-15.24t(29.2)	-39.86s		-111.51t(9.6)	-131.45t(9.4)	
$RuI_3(NO)((p\text{-}Me_2NPh)Et_2P)_2$	-9.18s	-20.69t(31.2)	-39.85s		-111.23t(8.6)	-131.54t(9.6)	
$RuBr_3(NO)((p\text{-}ClPh)Et_2P)_2$	-7.90s	-15.13t(29.6)					
	-7.53s	-14.40t(29.6)		-149.79d(11.6)	-128.9t (8.6)	-131.79t(8.4)	-187.9s
$RuCl_3(NO)(Et_2PhP)_2$	-7.4s	-12.6t (30.0)			-128.7t(8.0)	-130.3t (8.0)	-130.3s
$RuBr_3(NO)(Et_2PhP)_2$	-8.0s	-14.93t(29.4)		-151.85s [b]	-128.5t(9.2)	-130.26s	-130.18s
$RuI_3(NO)(Et_2PhP)_2$	-9.17s	-20.40t(32.8)			-128.3t(7.2)	-130.28s	-130.07s

(a) chemical shifts in ppm downfield from TMS
coupling constants (Hz) in parentheses
s = singlet; d = doublet; t = triplet

(b) observed on addition of $Cr(acac)_3$

FIGURE 4·4

^{13}C NMR SPECTRA: $RuX_3(NO)L_2$ COMPLEXES WHERE L = $(p\text{-}Me_2NPh)Et_2P$



substituent) and this is manifested in a shielding effect of the protons in this position. There is no change in the coupling constants associated with either resonance multiplet with change in halogeno-ligand, and only minor deshielding of the ortho protons with such change (Table 4.10).

The familiar deshielding of the methylene multiplet of the ethyl groups with halogen charge in the order Cl,Br,I is again observed here. Change in para-substituent on the phenyl ring does not lead to a significant change in the degree of this deshielding, within the uncertainty of measurement ($\pm$ 0.01 ppm). The deshielding phenomenon can no doubt be rationalised as discussed previously (Chapters 2 and 3).

(d) ^{13}C NMR spectra :-

The complexes $RuBr_3(NO)((p\text{-}ClPh)Et_2P)_2$ and $RuX_3(NO)((p\text{-}Me_2NPh)Et_2P)_2$ (X = Cl,Br,I) have had ^{13}C spectra recorded in this work. The spectra obtained are listed in Table 4.11 and the p-Me_2N spectra are given in Fig. 4.4. The measurement uncertainty in the chemical shifts of these complexes is $\pm$ 0.02 ppm.

The spectra of the $(p\text{-}Me_2NPh)Et_2P$ complexes show a singlet for the methyl carbon and a triplet for the methylene carbon of the ethyl groups. The methyl carbons on the para-substituent give rise to a sharp singlet resonance which is practically invariant with change in halogeno-ligand.

The phenyl region resonances provide a good example of the mesomeric effect of the para substituent. Thus the meta carbon atoms are quite considerably shielded compared with their chemical shift in complexes of the unsubstituted ligand (Table 4.11). The ortho carbons are slightly deshielded in comparison with

TABLE 4.12

^{31}P NMR spectra of $RuX_3(NO)L_2$ complexes [a]

Compound	Chemical shift
$RuCl_3(NO)(Et_2PhP)_2$	-12.5
$RuBr_3(NO)(Et_2PhP)_2$	- 4.0
$RuI_3(NO)(Et_2PhP)_2$	+10.0
$RuCl_3(NO)((p\text{-}Me_2NPh)Et_2P)_2$	- 9.6
$RuBr_3(NO)((p\text{-}Me_2NPh)Et_2P)_2$	- 2.0

(a) chemical shifts in ppm relative to 85% H_3PO_4

complexes of Et_2PhP. These observations are predictable in terms of the mechanism of mesomeric electron release which will deshield the ortho carbon (meta to the substituent) and, conversely, shield the meta carbon.

The C_1 carbon atom (directly bound to the phosphorus atom) gives a measurable resonance for the chloro complex, but only on addition of tris(acetylacetonato)chromium (III). The resonance of this carbon is not observed for the bromo and iodo complexes, even after addition of the relaxation agent.

Both methyl and methylene carbons undergo a deshielding on halogen change in the order Cl,Br,I. The relative extent of this effect is similar to that found for ^{13}C spectra of Et_2PhP complexes (Table 4.11). However, for the methylene multiplet it is noticeable that the deshielding for the chloro complex with $(p\text{-}Me_2NPh)Et_2P$ as ligand is some 0.30 ppm greater than the analogous multiplet in the unsubstituted complex. This difference is similar for the bromo and iodo complexes of the two ligands. The possible cause of this effect is considered in the discussion of electronic spectra of these complexes.

(e) ^{31}P NMR spectra :-

Because of solubility problems discussed previously (p. 148) the ^{31}P NMR spectra of only two complexes $(RuX_3(NO)((p\text{-}Me_2NPh)Et_2P)_2$ (X = Cl,Br) could be obtained here.

It is of some interest that in otherwise analogous complexes of Et_2PhP and $(p\text{-}Me_2NPh)Et_2P$ the ^{31}P resonance is further upfield for the para-substituted ligand (Fig. 4.12). This is consistent with a relative shielding for ^{31}P nuclei in complexes of the $p\text{-}Me_2N$ ligand as compared with Et_2PhP, and this may be expected on the basis of mesomeric release of electrons

TABLE 4.13

Electronic absorption spectra [a] of $RuX_3(NO)L_2$ complexes where

$L = (p\text{-}QPh)Et_2P$: $Q = MeO, Me_2N, Cl, H$

Compound Q	X	halogen → metal $X_{nb} \longrightarrow eg^*$	phosphine → metal $P_{nb} \longrightarrow eg^*$	intra-ligand	Other bands
p-Me_2N	Cl	365 sh (7,000)	261 (25,000)	320 (18,000)	
	Br	384 sh (5,000)	263 (23,000)	305 (19,000)	
	I	430 sh (4,500)	263 (31,000)	305 (16,000)	
		351 sh (10,000)			
p-MeO	Cl	331 (6,900)	243 (14,000)	291 (20,500)	
	Br	350 sh (5,000)	242 (7,300)	301 (17,500)	
	I	422 sh (3,100)	252 (18,000)	(c)	
		343 (5,200)			
p-H	Cl	320 (9,000)	(b)	285 (15,000)	
	Br	342 (6,000)	(b)	295 (15,000)	
	I	360 (1,500)	(b)		258 (5,500)
p-Cl	Cl	318 (10,000)	(b)	286 (15,000)	
	Br	335 (6,000)	(b)	293 (14,000)	

(a) wavelengths in nanometres
extinction coefficients in parentheses sh = shoulder
(b) not observed because of solvent restrictions (see text) (c) not observed

FIGURE 4·5

ELECTRONIC SPECTRA OF $RuCl_3(NO)L_2$ COMPLEXES WHERE L IS A PARA-SUBSTITUTED PHENYLDIETHYLPHOSPHINE

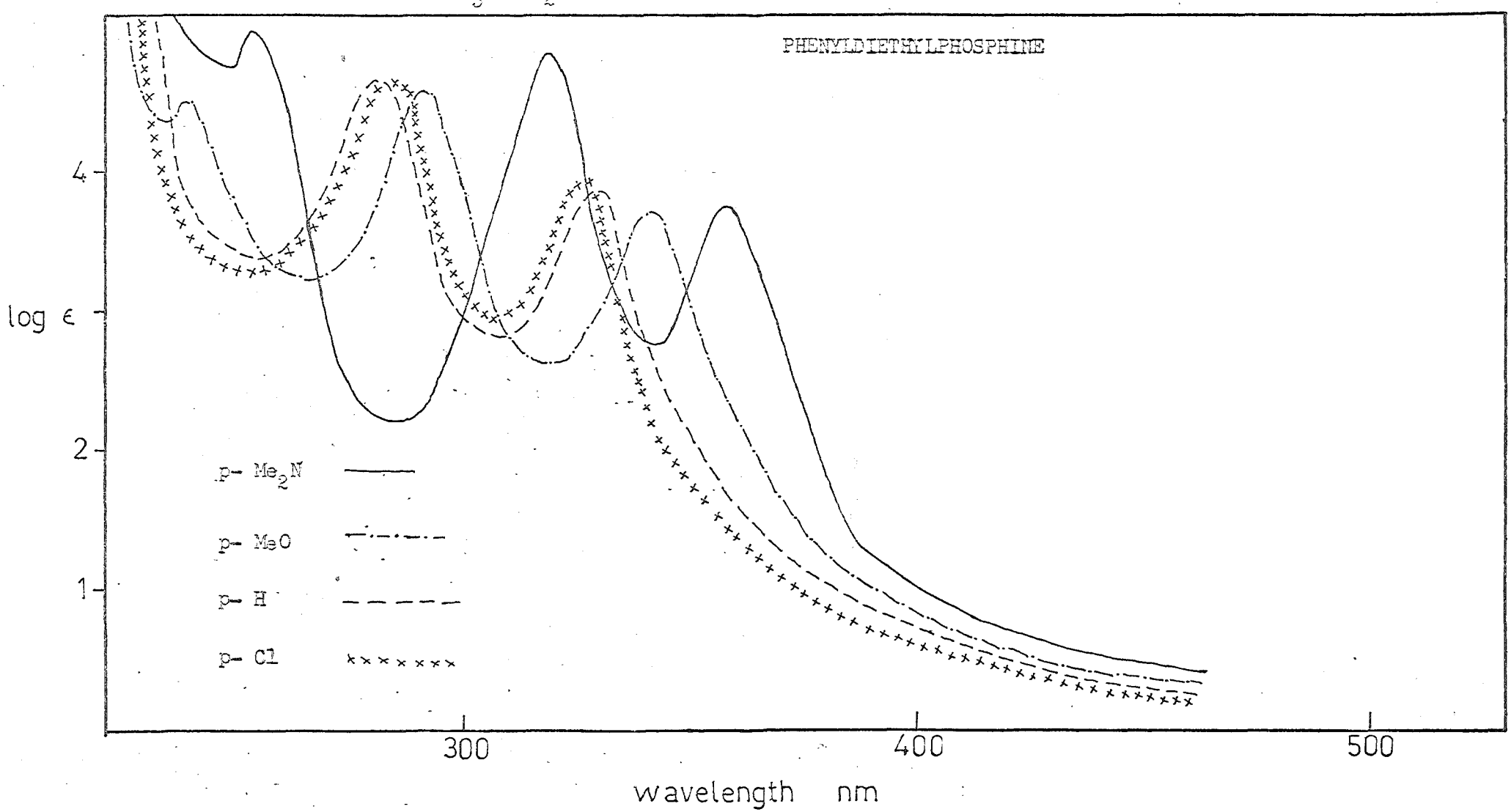
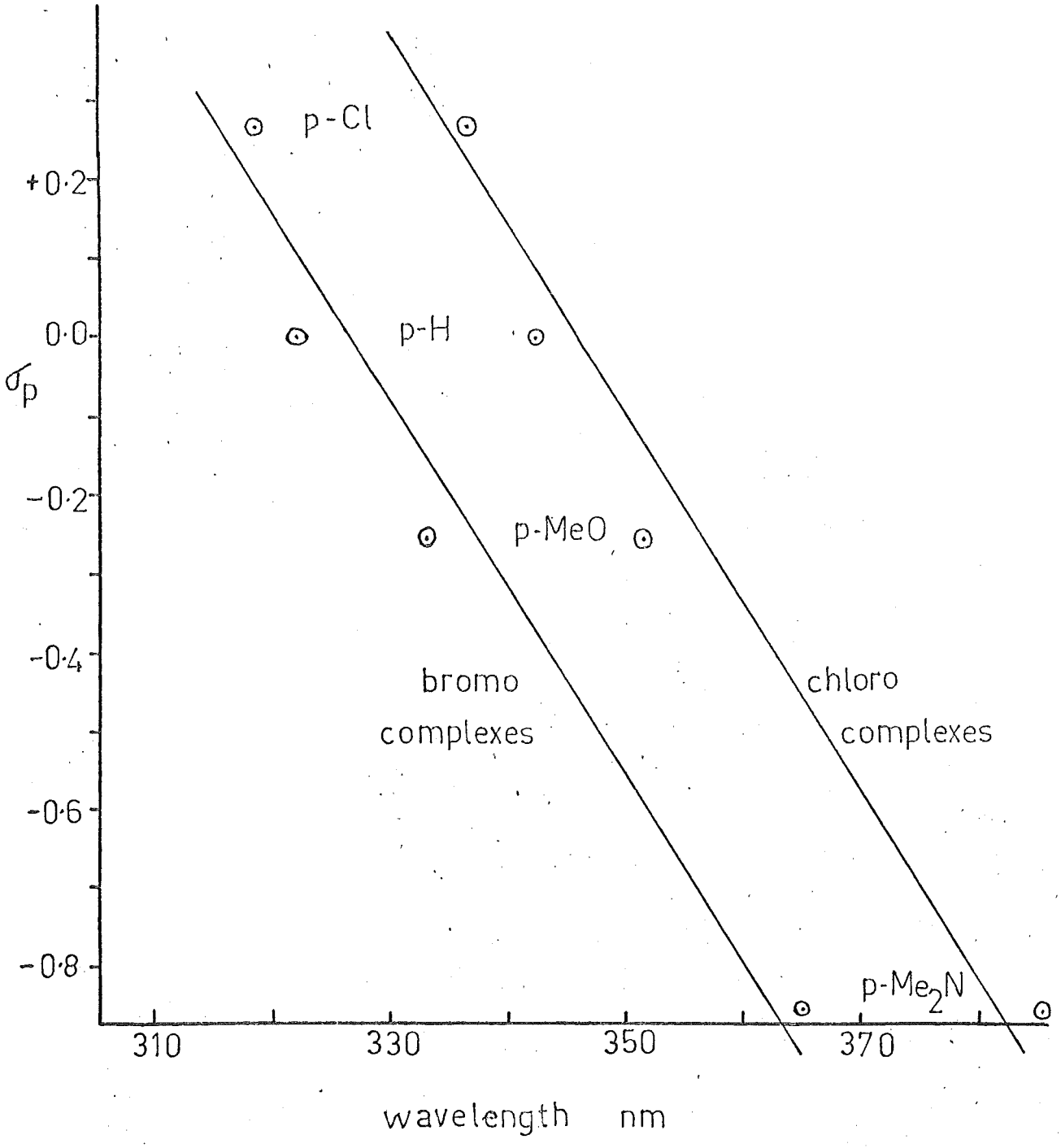


FIGURE 4·6

CORRELATION OF σ_p WITH THE HALOGEN TO METAL CHARGE TRANSFER TRANSITION IN p-SUBSTITUTED $RuX_3(NO)L_2$ COMPLEXES



from the p-Me_2N substituent and a consequent further shielding of the phosphorus nucleus.

(f) Electronic absorption spectra :-

The lowest energy charge transfer transition in these spectra is intense ($\epsilon > 5,000$), and this band obscures the ligand field transitions of the ruthenium (II) metal ion. The spectra are devoid of absorption from 500 nm to 1200 nm which suggests that the spin-allowed ligand field bands occur at higher energy than 500 nm and hence are masked by the rather broad lowest energy charge transfer transition.

The spectra are still, however, of interest (Table 4.13, Fig. 4.5). A band near 350 nm which decreases in energy with change of halogeno-ligand in the order Cl,Br,I (decreasing electron affinity) may, as before, be assigned to a halogen to metal charge transfer transition. This band varies in energy with change in para-substituent on the diethylphenylphosphine ligand in a manner which can be correlated, at least approximately, with the σ_p substituent constants for the para substituents (Figure 4.6). This correlation is similar for chloro and bromo complexes. However, for the iodo complexes the halogen to metal charge transfer transition consists of two components and the corelation with σ_p cannot be satisfactorily investigated.

The energy of the halogen to metal charge transfer transition is lowest for the p-Me_2N substituted complexes (Table 4.13). Since the transition can be considered to terminate on the e_g^* orbitals it appears that the para-substitients decrease the energy of these orbitals in proportion to their electronic effect as measured by the σ_p substituent constant.

The phosphine to metal charge transfer transition can only

be assigned for p-MeO and p-Me_2N substituted complexes (Table 4.13). For p-Cl and p-H as substituents the energy of this band is apparently too high to allow its measurement. The region of the spectrum below 240 nm cannot be investigated because the solubility problems, apparent for Et_2PhP and PEt_3 complexes (see earlier), again occur for the p-substituted complexes discussed here. The complexes are insoluble in any suitable solvent which is transparent in the higher energy ultra-violet region.

The phosphine to metal charge transfer transition is observed around 243 nm (p-MeO substituent) and 263 nm (p-Me_2N substituent). It seems probable that the analogous transition in p-Cl and Et_2PhP complexes occurs at even lower energy. This is therefore a similar situation to that discussed above for the halogen to metal charge transfer transition, and can be rationalised on the basis of the change in energy of the e_g^* orbitals with change in para substituent.

The other region of charge transfer absorption occurs around 300 nm (Table 4.13). The variation of this band with change in halogen does not produce a consistent trend in energy change. The free phosphine ligands have an intra-ligand transition in this region and thus it seems likely that the observed transitions in the complexes correspond to such a transition. There may be an alternative possibility that the band corresponds to a transition between the metal ion and the nitrosyl ligand although there can be no firm evidence that this is so. There is an approximate correlation of the energy of the band with the σ_p substituent constants for the p-substituents.

On the basis of the results found for the halogen to metal charge transfer transition in particular, and probably for

the phosphine-metal charge transfer transition as well, it seems that change in para substituent influences the energy of the e_g^* orbitals of the metal ion and that this effect is greatest (i.e. largest decrease in energy) for the strongest +R substituent (p-Me_2N). In this respect it is unfortunate that the ligand field transitions for these complexes could not be observed since these should occur at progressively lower energy for p-MeO and p-Me_2N substituents if the above premise is correct.

Assuming that the energy of the e_g^* orbitals is indeed decreased by + R para-substituents this might imply an increased possibility of the mixing of a paramagnetic electronic state with the ground state (diamagnetic) configuration. Further this paramagnetic contribution would be expected to increase with change in halogen in the order Cl,Br,I since this order is also that of decreasing ligand field for these halogeno-ligands. (An earlier discussion has been made on this subject, pp. 46,47).

Thus the possibility of a small NMR contact shift as a result of a paramagnetic contribution to the ground state electronic configuration should be greatest for the p-Me_2N substituent. It can be recalled from above (p. 157) that comparison of ^{13}C NMR spectra of (p-Me_2NPh)Et_2P and Et_2PhP complexes showed a larger methylene carbon deshielding for complexes of the former ligand by c.a. 0.30 ppm for all three halogeno-ligands. This therefore might give support to the above premise in terms of a paramagnetic contribution to the ground state configuration.

SECTION 4.4 EXPERIMENTAL

A. Discussion

(i) Preparation of ruthenium (II) complexes :-

The preparation of ruthenium (II) complexes of general formula $RuX_3(NO)L_2$ (X = Cl,Br,I ; L = PEt_3, Et_2PhP or a para-substituted phenyldiethylphosphine) involved reaction of $RuCl_3(NO)$ (prepared as detailed on p. 187) with the phosphine ligand in boiling 2-methoxyethanol. This gave the chloro complexes, $RuCl_3(NO)L_2$, and the bromo and iodo complexes were prepared by metathetical reaction with lithium bromide or sodium iodide respectively.

(ii) Attempts to nitrate the phenyl ring of trichloronitrosylbis(diethylphenylphosphine) ruthenium(II) :-

Attempts were made to bring about the nitration of the phenyl ring of the ligand diethylphenylphosphine (=L) in the complex, $RuCl_3(NO)L_2$, but although some promising results were obtained no products could be identified. It is not possible to obtain the nitro-substituted ligand by Friedel-Crafts reaction of phosphorus trichloride and p-nitroaniline followed by a Grignard reagent substitution, as has been successfully accomplished for p-methoxy and p-dimethylamino analogues in the present work (see p. 182). The Grignard conversion of the dichlorophosphine intermediate to the diethylphosphine group will no doubt proceed but the nitro group on the phenyl ring will also react with the Grignard reagent[209]. Thus it was decided to attempt a direct nitration of the ligand in its coordinated state.

The following systems were tried, in order of increasing activity of the nitrating agent :

(a) fuming nitric acid in acetic anhydride

(b) 1:1 nitric acid/sulphuric acid dropped onto a solution of $RuCl_3(NO)(Et_2PhP)_2$ in nitromethane boiling under reflux

(c) direct reflux of $RuCl_3(NO)(Et_2PhP)_2$ in 1:3 nitric acid/sulphuric acid as the solvent

Method (a) gave no reaction in the cold or with shaking for some hours, but on boiling under reflux for some time an orange material was obtained in which the position of the nitrosyl stretching frequency in the infra-red spectrum had shifted to around 1900 cm^{-1} (from 1860 cm^{-1}). However, there were no nitro group absorptions in the infra-red spectrum so this method was not persevered with.

Method (b) resulted in a water-soluble product which probably occurred through protonation of the phosphine. Once again, however, no nitro group absorptions were observed in the infra-red spectrum.

Method (c) gave a lemon-yellow oily material which again appeared to be a protonation product since it was water-soluble. This time the infra-red spectrum showed nitro absorptions around 1520 cm^{-1}, albeit ill-defined.

The system was not further investigated as it appeared unlikely that the reaction products would, in fact, be the molecular species $RuX_3(NO)((p\text{- or } m\text{-}\ NO_2Ph)Et_2P)_2$ required for the general study of para-substituted phosphine ligands.

It is, however, of some interest that the complex, $RuCl_3(NO)(Et_2PhP)_2$ does not undergo even partial degradation under

the extreme acidic conditions employed. It also appears that the phenyl ring is substantially deactivated towards electrophilic attack, upon coordination, since free benzene can, of course, be readily nitrated under the conditions of methods (b) and (c).

(iii) An attempt to employ p-dimethylaminophenyldiethyl phosphine as a bidentate ligand :-

The ligand, $(p\text{-}Me_2NPh)Et_2P$, is potentially a bidentate ligand since, as well as a phosphorus donor atom, it also contains a nitrogen atom, and this is some distance removed from the phosphorus. Thus, the coordination of both phosphorus and nitrogen atoms to the same metal ion should be feasible.

In the preparation of mononuclear ruthenium nitrosyl complexes, to be described shortly, the ligand was added in excess to the trichloronitrosylruthenium solution. If, however, the amount of phosphine is reduced so that the molar ratio is 1:2 of phosphine to $RuCl_3(NO)$ this would be expected to favour any tendency of the ligand to coordinate in a bidentate manner.

Using this ratio, a brown powder was obtained after boiling the reactants under reflux for 2 hours in 2-methoxyethanol. This brown material proved to be insoluble in all common organic solvents; hence NMR identification was precluded. An infra-red spectrum showed a broad, split nitrosyl stretching absorption around 1860 cm^{-1} and the presence of characteristic phosphine absorptions. The analytical figures obtained for the product were C = 14.9% and H = 2.37%. A dimer of formula $Ru_2Cl_6(NO)_2(phosphine)_2$, and in general the polymer $[RuCl_3(NO)(phosphine)]_n$, requires C = 32.0% and H = 6.7%.

The brown material obtained above was boiled under reflux with excess of phosphine to give an orange solution. However, no

solid could be obtained from the oil remaining after solvent removal, and an infra-red spectrum of the oil, although having a nitrosyl absorption and phosphine bands, was quite distinct from the infra-red spectrum of the mononuclear complex with the ligand coordinated in the monodentate manner.

It seems probable that the phosphine can coordinate in a bidentate fashion, although the nature of the polymeric material so formed cannot be deduced from the available information. It is not likely that any rearrangement or degradation of the ligand has occurred, since the ratio of hydrogen to carbon in the free phosphine is calculated to be 1: 7.2, and that deduced from the analytical figures given above for the brown polymeric reaction product is 1:6.6.

B. Experimental details for preparation of ruthenium (II) nitrosyl complexes

The complexes, $RuCl_3(NO)L_2$ (L = tertiary phosphine), were prepared by the method given below for the diethylphenylphosphine complex, as a general example.

Trichloronitrosylbis(diethylphenylphosphine)ruthenium(II)[205], $RuCl_3(NO)(Et_2PhP)_2$

$RuCl_3(NO)$hydrate (1gm) was dissolved in 2-methoxyethanol (25 ml) and boiled under reflux. Et_2PhP (2.5 gm) was added and the mixture refluxed for a further 10 minutes. The solution was filtered and evaporated to dryness to give a brown oil. This was treated with methanol (15 ml) and cooled in an ice bath. The result was the deposition of orange-brown needles of the required complex (2.3 gm, 84%). m.pt. 157 - 162° c f. lit.[205] 167 - 168° ν(NO) at 1856 cm^{-1} c.f. lit.[205] 1863 cm^{-1}. Analysis : Calculated for $C_{20}H_{30}Cl_3NOP_2Ru$, C = 42.1%; H = 5.26%. Found : C = 42.0% H = 5.44%.

The bromo and iodo complex were obtained from the chloro complex by metathesis, as follows.

Tribromonitrosylbis(diethylphenylphosphine)ruthenium(II)[205], $RuBr_3(NO)(Et_2PhP)_2$

The trichloro complex prepared above and lithium bromide, in 1:10 molar ratio, were dissolved in 2-methoxyethanol and boiled under reflux for 10 minutes. After evaporation to dryness under reduced pressure the solid residue was washed with hot water. The complex was recrystallised from chloroform to give brown microcrystals (70%). m.pt. 159 - 160° c.f. lit.[205] 161-163°. ν(NO) at 1852 cm^{-1} c.f. lit.[205] 1850 cm^{-1}. Analysis : Calculated for $C_{20}H_{30}Br_3NOP_2Ru$, C = 34.1%; H = 4.26%. Found : C = 33.8%; H = 4.12%.

Triiodonitrosylbis(diethylphenylphosphine)ruthenium(II)[205], $RuI_3(NO)(Et_2PhP)_2$

The trichloro complex and sodium iodide, in molar ratio 1:10. were reacted as for the tribromo analogue. The red product was recrystallised from chloroform to give a microcrystalline dark red compound (74%). m.pt. 179 - 181° c.f. lit.[205] 184 - 188°. ν(NO) at 1848 cm^{-1}. Analysis : Calculated for $C_{20}H_{30}I_3NOP_2Ru$, C = 28.4%; H = 3.56%. Found : C = 28.5%; H = 3.59%.

The following compounds were similarly prepared

(i) With triethylphosphine

Trichloronitrosylbis(triethylphosphine)ruthenium(II)[204], $RuCl_3(NO)(PEt_3)_2$

Brown needles, from chloroform-methanol (87%). m.pt. 128 - 129°. c.f. lit.[204] 128-130°. ν(NO) at 1830 cm^{-1} c.f. lit.[204] 1829 cm^{-1}. Analysis : Calculated for $C_{12}H_{30}Cl_3NOP_2Ru$,

C = 30.6%; H = 6.38%. Found : C = 30.6%; H = 6.45%.

Tribromonitrosylbis(triethylphosphine)ruthenium(II), $RuBr_3(NO)(PEt_3)_2$

Orange-brown needles, from chloroform (72%) m.pt. 124-125° ν(NO) at 1838 cm^{-1}. Analysis : Calculated for $C_{12}H_{30}Br_3NOP_2Ru$, C = 23.7%; H = 4.94%. Found : C = 23.9%; H = 5.20%.

Triiodonitrosylbis(triethylphosphine)ruthenium(II)[204] $RuI_3(NO)(PEt_3)_2$

Red microcrystals, from chloroform. (79%) m.pt. 118 - 120° ν(NO) at 1827 cm^{-1} c f. lit.[204] 1820 cm^{-1}. Analysis : Calculated for $C_{12}H_{30}I_3NOP_2Ru$, C = 19.2%; H = 4.01%. Found : C = 19.7%; H = 4.29%.

(ii) With p-methoxyphenyldiethylphosphine

Trichloronitrosylbis(p-methoxyphenyldiethylphosphine) ruthenium(II)[205] $RuCl_3(NO)((p\text{-}MeOPh)Et_2P)_2$

Orange-brown microcrystals, from chloroform-methanol (74%) m.pt. 157 - 159° c f. lit.[205] 173 - 175° ν(NO) at 1836 cm^{-1} c f. lit.[205] 1834 cm^{-1}. Analysis : Calculated for $C_{22}H_{34}Cl_3NO_3P_2Ru$, C = 41.9%; H = 5.40%. Found : C = 41.6%; H = 5.60%.

Tribromonitrosylbis(p-methoxyphenyldiethylphosphine) ruthenium(II), $RuBr_3(NO)((p\text{-}MeOPh)Et_2P)_2$

Brown microcrystals, from chloroform-methanol (70%). m.pt. 165 - 169°. ν(NO) at 1858, 1832 cm^{-1}. Analysis : Calculated for $C_{22}H_{34}Br_3NO_3P_2Ru$, C = 34.6%; H = 4.45%. Found : C = 34.7%; H = 4.49%.

Triiodonitrosylbis(p-methoxyphenyldiethylphosphine) ruthenium(II), $RuI_3(NO)((p\text{-}MeOPh)Et_2P)_2$

Red prisms, from chloroform-methanol (68%). m.pt. 158 - 161°. ν(NO) at 1850, 1842 cm^{-1}. Analysis : Calculated for $C_{22}H_{34}I_3NO_3P_2Ru$, C = 29.2%; H = 3.76%. Found : C = 28.8%; H = 3.61%.

(iii) With p-chlorophenyldiethylphosphine

Trichloronitrosylbis(p-chlorophenyldiethylphosphine) ruthenium (II), $RuCl_3(NO)$ $((p\text{-}ClPh)Et_2P)_2$

Yellow-orange powder, from chloroform. (47%). m.pt. 169 - 172°. ν (NO) at 1849 cm^{-1}. Analysis : Calculated for $C_{20}H_{28}Cl_5NOP_2Ru$, C = 37.6%; H = 4.39%. Found : C = 37.7%; H = 4.74%.

Tribromonitrosylbis(p-chlorophenyldiethylphosphine) ruthenium (II), $RuBr_3(NO)$ $((p\text{-}ClPh)Et_2P)_2$

Brown crystals, from chloroform. (75%). m.pt. 162 - 164° ν(NO) at 1847 cm^{-1}. Analysis : Calculated for $C_{20}H_{28}Br_3Cl_2NOP_2Ru$, C = 31.1%; H = 3.62%. Found : C = 31.3%; H = 4.30%.

The triiodo complex with $(p\text{-}ClPh)Et_2P$ as ligand could not be obtained in a pure state.

(iv) With p-dimethylaminophenyldiethylphosphine

Trichloronitrosylbis(p-dimethylaminophenyldiethyl phosphine)ruthenium(II), $RuCl_3(NO)$ $((p\text{-}Me_2NPh)Et_2P)_2$

Orange needles, from chloroform (48%). m.pt. 193 - 194° ν(NO) at 1839, 1829 cm^{-1}. Analysis : Calculated for $C_{24}H_{40}Cl_2N_3OP_2Ru$, C = 43.9%; H = 6.10%. Found : C = 44.0%; H = 6.23%.

Tribromonitrosylbis(p-dimethylaminophenyldiethylphosphine) ruthenium (II), $RuBr_3(NO)\ ((p\text{-}Me_2NPh)Et_2P)_2$

Orange-brown microcrystals, from benzene (75%). m.pt. 198 - 202°. ν(NO) at 1835, 1812 cm^{-1}. Analysis : Calculated for $C_{24}H_{40}Br_3N_3OP_2Ru$, C = 36.6%; H = 5.07%. Found : C = 36.9%; H = 5.22%.

Triiodonitrosylbis(p-dimethylaminophenyldiethylphosphine) ruthenium (II), $RuI_3(NO)\ ((p\text{-}Me_2NPh)Et_2P)_2$

Red microcrystals, from chloroform (70%). m.pt. 194 - 196° ν(NO) at 1822 cm^{-1}. Analysis : Calculated for $C_{24}H_{40}I_3N_3OP_2Ru$, C = 31.0%; H = 4.30%. Found : C = 31.8%; H = 4.55%.

TABLE 5.1

Far Infra-Red Spectroscopic Parameters for the Systems Studied in this Work [a]

Variable	Square Planar				tetrahedral	octahedral			oxo	nitrido
	Ni(II)	Pd(II)	cisPt(II)	trans-Pt(II)	Co(II)	Re(II)	Ru(II)	Ru(III)	Re(V)	Re(V)
d configuration	d^8	d^8	d^8	d^8	d^7	d^5	d^6	d^5	d^2	d^2
ν(M-Cl) trans to X	400	355	(b)	340	333	293	290	333 320	322	(b)
ν(M-Cl) trans to P	(b)	(b)	308 280	(b)	(b)	(b)	(b)	256	295	282
ν(M-Br) trans to X	337	270	(b)	252	260	215	226	282 247	212 196	(b)
ν(M-Br) trans to P	(b)	(b)	202 108	(b)	(b)	(b)	(b)	166	(b)	190
ν(M-I) trans to X	304	215	(b)	201	212	175	159	(b)	160 140	(b)
ν(M-I) trans to P	(b)	(b)	170 153	(b)	(b)	(b)	(b)	(b)	(b)	133
ν(M-X) trans to (NO, N^{3-}, O^{2-})						319 225 184	321 260 223		220 160	214 Cl 136 Br 94 I
ν(M-P) trans to P	262	235	(b)	223	248 225	232	245	(d)	270	242
ν(M-P) trans to X	(b)	(b)	(c)	(b)	(b)	(b)	(b)	250	270	(d)

(a) frequencies in cm^{-1} the parameters given in the table are averaged results
(b) not applicable for stereochemical reasons
(c) not justified in averaging widely divergent results (see Chapter 2)
(d) expected absorption not observed

TABLE 5.2

NMR Spectroscopic Parameters for the Systems Studied in this Work [a][c]

Variable		Square Planar				Tetrahedral	Octahedral			
		Ni(II)	Pd(II)	cisPt(II)	transPt(II)	Zn (II)	Re(II)	Ru(II)	oxo Re(V)	nitrido Re(V)
d configuration		d^8	d^8	d^8	d^8	d^{10}	d^5	d^6	d^2	d^2
δ CH3	^1H	-1.00	-1.10	-1.16	-1.15	-1.23	-1.25	-1.26		
δ CH2	^1H	-1.45	-1.99	-2.17	-2.12	-1.83	-2.05	-2.92(f) -2.42(g)	-2.34	-2.52(h) -3.13(i)
δ main phenyl	^1H	-7.87	-7.37	-7.49	-7.45	-7.41	-7.52	-7.40	-7.40	-7.35
δ ortho	^1H	(d)	-7.67	-7.58	-7.60	(e)	(e)	-7.64	-7.65	-7.53
δ CH3	^{13}C	(d)	- 8.4	- 8.1	- 8.2	-7.9	(d)	-7.8	-7.2	(c)
δ CH2	^{13}C	(d)	-16.9	-16.8	-15.5	-13.8	(d)	-16.5	-16.2	(c)
magnitude of deshielding [b]	^1H	(d)	0.42	0.17	0.38	0.03	(e)	0.42	0.27	0.25
	^{13}C	(d)	7.0	(d)	5.4	0.17	(d)	7.8	(e)	(e)

(a) NMR chemical shifts in ppm downfield from TMS
(b) defined as the difference in chemical shift for the methylene multiplet in chloro and iodo complexes
(c) results averaged over those for the three halogeno-ligands
(d) measurement not made (see text)
(e) expected parameter not observed
(f) Et_2PhP complexes
(g) PEt_3 complexes
(h) CH_2 *trans* phosphines
(i) CH_2 phosphines *trans* to halogen

CHAPTER 5

TRENDS IN SPECTROSCOPIC PARAMETERS AND THEIR RELATION TO THE NATURE OF THE METAL - HALOGEN AND METAL - PHOSPHORUS BONDS

For convenience in making comparisons of the various spectroscopic parameters obtained for the three systems described in Chapters 2, 3 and 4, Tables 5.1 and 5.2 contain a summary of the principal spectroscopic features and their values as obtained in the present work. In these tables trends can be investigated in terms of variation of metal ion, oxidation state, and stereochemistry. The effect of nitrosyl, nitrido and oxo ligands can also be compared. The parameter values given in Tables 5.1 and 5.2 are generally averaged over the results found for PEt_3 and Et_2PhP ligands.

SECTION 5.1 SPECTRAL PARAMETERS AND THEIR VARIATION BETWEEN SYSTEMS

(a) <u>The effect of changes in d electron configuration with constant oxidation state</u> :-

(i) <u>Infra-red parameters</u> It can be observed from Table 5.1 that for metal-halogen stretching vibrations the value of ν(M-X) is highest for the d^8 complexes, as compared with d^5 and d^6 complexes, for divalent metal ions of comparable mass. Thus a comparison can be made between palladium (II) and ruthenium (II), and platinum (II) and rhenium (II). The trend is consistent for the three halogeno ligands. It is not possible to know if the difference is caused by the different stereochemistries

involved, (i.e. square planar or octahedral), or whether it can be related to the higher d electron configuration. However, for both the d^8 configuration and square planar complexes π-bonding is expected to be a greater component of the metal-ligand bond than for metal ions with fewer d electrons and in octahedral coordination.

For the metal-phosphorus stretching frequencies there is very little difference between compounds. However, comparison of the data in Table 5.1 for ruthenium (II) and palladium (II) complexes (of similar mass) indicates that the Ru-P bond is stronger than the Pd-P bond. This is consistent with NMR results (see below). The influence of the nitrosyl ligand in the ruthenium (II) complexes may be the important factor here, viz. back bonding to the nitrosyl may have a significant influence on the Ru-P σ bond.

(ii) NMR results Unlike the situation for the infra-red spectra discussed above it is possible to compare NMR data for the complexes studied without any restrictions related to mass differences. Also the differences in the various metal ion radii are minor. The data of Table 5.2 have been obtained by averaging the results for chloro, bromo and iodo complexes.

For divalent metal ions the greatest deshielding of the methylene multiplet in the ^{1}H NMR spectra occurs for the nitrosyl complexes of ruthenium (II). This may be related to the ability of nitric oxide to form a metal to nitrosyl dative π-bond increasing the electropositive nature of the metal, with consequent deshielding of the protons. It is not possible to include the paramagnetic rhenium (II) complexes in this discussion, since although the ^{1}H NMR resonances for these compounds do not

appear to be grossly affected by paramagnetic contact shifts one cannot allow for this influence. The absence of large contact shifts in rhenium (II) compounds suggests that the unpaired electron is delocalized onto the non-phosphine ligands, in fact probably the nitrosyl.

The deshielding of the methylene multiplet increases in the ^{1}H NMR spectra with change in d^{8} metal ion from nickel to palladium to platinum. This was discussed in Chapter 2, Section 2.2.2, in terms of increasing metal to halogen $M_{d\pi} \longrightarrow X_{d\pi}$ bonding down the group.

The above observations for ^{1}H NMR spectra are not however supported by the results found for ^{13}C NMR spectra (see Table 5.2). This may suggest that the factors influencing chemical shifts are somewhat different for the two types of nuclei.

(b) The effect of changes in oxidation state :-

(i) Infra-red results The influence of the metal ion oxidation state is apparent in the metal - halogen stretching vibrations in the infra-red spectra. Thus it can be seen from Table 5.1 that for analogous vibrations in ruthenium (III) and ruthenium (II) complexes the higher frequency occurs for ruthenium (III). This is a direct reflection of the greater electrostatic effect of the higher charge on ruthenium in the trivalent state.

A similar comparison can be made between rhenium (II) and (V), at least for the chloro complexes; the frequencies of Re-Cl stretching vibrations in complexes of pentavalent rhenium are higher than for the divalent complexes. However, for the bromo analogues the frequencies are similar in the two cases and for the iodo complexes the frequencies are now higher for

rhenium (II). Electrostatic effects are likely to be more important for the chloro ligands and progressively less for bromo and iodo ligands and hence it might be tentatively suggested that the relative increase in metal - halogen frequencies in the divalent bromo and iodo complexes could be related to the influence of $Re_{d\pi} \longrightarrow X_{d\pi}$ bonding, which may be invoked for the d^5 rhenium (II) metal ion but is expected to be unlikely for the d^2 rhenium (V) ion. As pointed out in Chapter 3, Section 3.1 however, the lower symmetry of the oxo complexes may result in coupling of vibrational modes and hence any deductions based on vibrational frequencies found for these complexes can only be tentative.

(ii) NMR spectra Change in oxidation state has an effect on the initial deshielding of the methylene multiplet in the ^1H NMR spectra of the complexes studied in this thesis. Thus, as can be seen in Table 5.2, the methylene multiplets of the phosphine ligands in rhenium (V) complexes resonate at lower field than for the analogous multiplet in square planar complexes with divalent metal ions. This can be related to the effect of the greater effective positive charge on rhenium which will have a considerable electrostatic effect on the charge distributions within the phosphine ligands. Charge draw-off to the pentavalent metal ion upon coordination may be expected to be greater than the similar electrostatic effect in complexes of divalent metal ions. Ruthenium (II) cannot be included in this particular discussion because of the effect of the nitrosyl ligand noted previously. The above suggestion is supported by the high infra-red stretching frequency of the rhenium - phosphorus bond, although coupling of vibrational modes may act to increase this frequency.

The magnitude of the deshielding of the methylene multiplet with change in halogen in the order Cl,Br,I shows a significant trend (Table 5.2). Thus for the d^8 and d^6 metal (II) complexes this parameter, "magnitude of deshielding", (defined as the difference between the methylene chemical shift in chloro and iodo complexes) is a maximum (c.a. 0.4 ppm) while for the d^2 rhenium (V) oxo and nitrido complexes the value of this parameter drops to 0.27 and 0.25 ppm respectively. A possible explanation for this trend may be that the influence of $M_{d\pi} \longrightarrow X_{d\pi}$ bonding is expected to be greater in the d^8 and d^6 complexes than in the d^2 complexes. Thus change in halogen in the d^8 and d^6 complexes produces a relatively large change in the methylene multiplet deshielding through the π-bonding mechanism proposed above, with its consequent influence on charge draw-off from the phosphine ligands. The low value of 0.03 ppm for the zinc (II) complexes is relevant in this context.

(c) Influence of nitrosyl, oxo and nitrido ligands :-

The metal - halogen bond *trans* to nitrosyl is found to be stronger than the other metal - halogen bonds in the complex. This has been discussed in Chapter 4 in terms of the enhancement of halogen to metal σ bonding by back-donation to the *trans* nitrosyl. In contrast to this effect, the oxo and nitrido ligands have a significant *trans* - labilising influence (Chapter 3) because of the effect of their strong dative σ and π bonding on the *trans* halogeno - ligand.

(d) The electronic effects of para-substituents on the phenyl ring of phenyldiethylphosphine complexes :-

As discussed in Chapter 4, the parasubstituents on the phenyl ring of the Et_2PhP ligand should influence the electronic environment of the metal ion in complexes of these ligands. That

this is true is shown by the effect on such spectroscopic parameters as the infra-red nitrosyl stretching frequency (p.153) and the metal - halogen stretching frequencies of the bond trans to the nitrosyl ligand in these complexes. However, the use of these ligands has been of little assistance in resolving interpretations of the nature of the metal - halogen bond. In retrospect, the electronic effects of para-substituents may have been better investigated by studying complexes of p-substituted diphenylethylphosphine ligands, where the effect on spectroscopic parameters would presumably be enhanced.

SECTION 5.2 INTERPRETATION OF SPECTROSCOPIC MEASUREMENTS

(a) NMR chemical shifts :-

The observed deshielding of the phosphine ligand methylene multiplets with change in halogen in the ^{1}H and ^{13}C NMR of complexes of diamagnetic metal ions studied in this work may be explained in a number of ways (Chapter 2). Briefly these are :

(1) The magnetic effect of halogen lone pairs on the organic groups of the phosphines.

(2) The influence of metal to halogen $M_{d\pi} \longrightarrow X_{d\pi}$ bonding on the metal ion and hence, by charge draw-off, on the phosphine ligands.

(3) Polarisation of the halogen valence electrons with consequent increase in the electropositive nature of the metal ion and, again, charge draw-off from the phosphine ligands.

(4) The effect of paramagnetic contact interactions arising from some mixing of excited electronic states with the diamagnetic ground electronic state.

The explanations (1) and (3) above can be considered as less likely than the other two, mainly on the basis of the results found for zinc (II) complexes. In the ^{1}H and ^{13}C NMR of zinc complexes studied in this work there is, at best, a marginal deshielding of the phosphine ligand methylene protons (or carbon atoms) on change of halogen. It is probable that polarisation effects will be similar for both transition and non-transition metal ions and this suggests that the polarisation explanation is of minor importance (this effect may in fact be the cause of the very minor deshielding changes observed for the zinc complexes). The effect of magnetic interactions of halogen lone pairs can also probably be discounted, even though the zinc complexes are pseudo-tetrahedral and hence less susceptible to intramolecular effects than square planar or octahedral complexes. As discussed in Chapter 2 the stereochemical differences are probably not great enough to make intramolecular magnetic interactions negligible in the zinc complexes, if this was the cause of the observed deshielding changes.

The explanation in terms of a contribution to the ground state configuration from low lying paramagnetic excited states can only be advanced as a premise in the work because in only one case, the binuclear platinum (II) complexes, can a correlation of chemical shift changes and the energy gap between ground and excited states (as measured by the energy of ligand field transitions) be made. Although this correlation (Fig. 2.14) is good it can hardly be considered as extensive evidence for the contribution of this effect to the observed deshielding.

The explanation in terms of the influence of metal - halogen $M_{d\pi} \longrightarrow X_{d\pi}$ bonding receives support from a number of observations (see discussion, Chapter 2). It is significant

that the results from ^{1}H, ^{13}C and ^{31}P NMR can all be considered to support this explanation (see p.149), even though the chemical shift trends for ^{1}H and ^{13}C NMR are the opposite to those found in ^{31}P NMR spectra with change of halogen in these complexes. If the paramagnetic contact contribution explanation was valid a deshielding of ^{31}P resonances with change in halogen might be expected, rather than the shielding which is in fact observed.

(b) Comparison of infra-red and NMR measurements :-

In general it may be said that infra-red stretching frequencies give information about the overall bond strength of bonds between two nuclei, without differentiating specifically between components of such bonding. NMR chemical shift trends measure changes in electron density at the particular nucleus under study. As related to the present study these two techniques give what appear to be conflicting results in terms of the strength of the metal - phosphorus bond. The situation is clearest for trans square planar complexes, where infra-red data show a small but significant decrease in metal - phosphorus stretching frequency (and hence, presumably, bond strength) with change in halogen in the order Cl,Br,I, (ignoring possible mass effects caused by change of halogen) whereas the NMR chemical shift changes suggest an increasing component of electron drift from the organic ligands towards the metal ion, and hence presumably into the metal-phosphorus bond, with consequent enhancement of the σ bond strength. It is significant that this apparent impasse cannot be resolved by invoking pure σ bonding as the total covalent contribution to the metal-phosphorus bond. However, if $d\pi$ - $d\pi$ back-bonding between metal and phosphorus

is considered then the apparent conflict between the two techniques can be interpreted as follows.

The influence of $M_{d\pi} \longrightarrow X_{d\pi}$ bonding between the metal ion and the halogeno-ligands may be considered to become more important in the order chlorine < bromine < iodine. Therefore the amount of metal ion charge available for $d\pi - d\pi$ bonding between metal and phosphorus will decrease in this same order. Thus the action of the metal-phosphorus π-bond in partially neutralising the positive charge induced on phosphorus upon coordination will be less effective as the halogeno-ligand changes in the order Cl,Br,I, and hence charge draw-off from the organic groups on phosphorus will increase as the halogen changes as above. This explains the chemical shift trends found for ^{1}H, ^{13}C and ^{31}P NMR. Further, since $d\pi - d\pi$ bonding between metal and phosphorus decreases, by the above explanation, as the halogen changes from chlorine to bromine to iodine, then the marginal decrease in metal-phosphorus bond strength with halogen change in this order may also be explained.

SECTION 5.3 THE NATURE OF THE METAL - HALOGEN AND METAL - PHOSPHORUS BONDS

The results found in this thesis lead to the following conclusions about the nature of the metal - halogen bond

(1) For complexes with an electronic configuration $\geqslant d^6$, results from both NMR and infra-red spectroscopy can be interpreted as supporting the importance of $M_{d\pi} \longrightarrow X_{d\pi}$ bonding as a component of the metal - halogen bond.

(2) Changes in oxidation state have a significant effect on spectroscopic parameters, particularly infra-red metal - halogen stretching frequencies, and this suggests that the ionic component of the metal - halogen bond is important, particularly for chloro ligands.

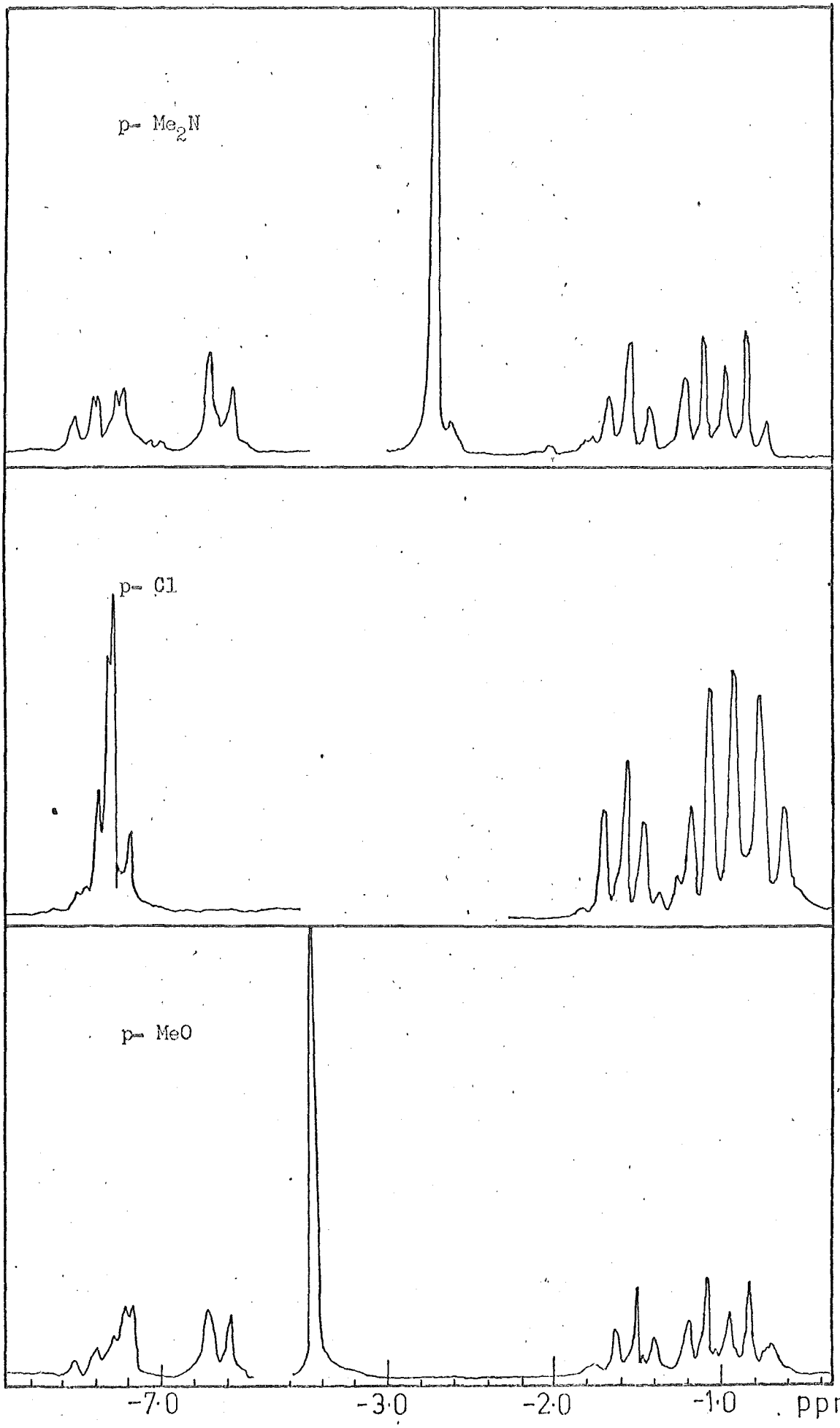
(3) For many of the systems studied in this work the occurrence of $X_{p\pi} \longrightarrow M_{d\pi}$ bonding would be expected to be negligible. Only for the complexes of rhenium (V) with the d^2 electron configuration would this component of π-bonding be expected to be important, but the strong dative σ and π-bonding of the oxo and nitrido ligands in these complexes will act to offset this. In any case, the techniques used in this work do not readily distinguish between halogen to metal σ donation, or $X_{p\pi} \longrightarrow M_{d\pi}$ electron donation in the same direction, and hence little can be said about the status of this particular halogen to metal π-bonding component.

(4) Many results found in this work markedly effect the metal - halogen σ bond, which is probably the major component of the total metal - halogen bond.

For the metal - phosphorus bond $d\pi - d\pi$ back-bonding may be considered to be important in resolving the paradox between infra-red and NMR measurements, and in explaining the labile nature of the phosphine ligands in complexes of nickel (II) and zinc (II), compared with similar complexes of palladium (II) and platinum (II), as discussed in Chapter 2.

FIGURE 6·1

^{1}H NMR SPECTRA OF p-SUBSTITUTED PHENYLDIETHYLPHOSPHINE LIGANDS



CHAPTER 6

PREPARATION OF LIGANDS AND STARTING MATERIALS, AND EXPERIMENTAL METHODS

SECTION 6.1. PREPARATION OF PHOSPHINE LIGANDS

The Grignard reaction of ethylmagnesium bromide with phosphorus trichloride or dichlorophenylphosphine was the preparative route used to obtain triethylphosphine or diethylphenylphosphine respectively.

For the para-substituted diethylphenylphosphine ligands it was necessary to prepare first the appropriate para-substituted dichlorophenylphosphine.

The reactions were carried out under a dry dinitrogen atmosphere at all times, and for Grignard reactions all glassware was scrupulously oven-dried and cooled in a stream of dry air.

(a) Triethylphosphine, PEt_3

(i) Grignard Method[46,212,213] Dry magnesium turnings (46.8gm, 2 moles) were placed in a 2 litre, 3-necked round flask, fitted with a stirrer, dinitrogen inlet, reflux condenser, and a dropping funnel. Dry ether (100 ml) was run in followed by ethyl bromide (1 ml). A crystal of iodine was dropped into the local concentration of ethyl bromide and the reaction initiated by the warmth of the hand. When the colour of the iodine began to be discharged the stirrer was started and ethyl bromide (218gm, 2 mole) in ether (300 ml) was run in at such a rate as to maintain a gentle reflux. At the end of this addition the solution was a clear black in colour with a little unreacted magnesium remaining. A further ether addition (100 ml) was made to replace that carried out

in the dinitrogen stream during reflux.

The next phase of the reaction was carried out at approximately -40° with cooling from a dry ice - acetone bath. Previously distilled phosphorus trichloride (80gm, 0.68 mole) in ether (150 ml) was added dropwise with rapid stirring over a three hour period. Phosphorus tribromide could be used, with no effect on the yield. During this addition the reaction was vigorous and a white or yellow solid separated. Sufficient stirring kept this from settling on the sides of the flask. If this occurred it was found that the yields were lower; this was presumably because local heating could then take place, leading to inefficiency in the phosphorus trihalide/Grignard reagent coupling reaction. The same effect was noted when the temperature was lowered to the point where the Grignard reagent solidified on to the flask walls. After completion of the phosphorus trihalide addition the white opalescent solution was allowed to warm up to room temperature.

Hydrolysis was carried out by addition of ammonium chloride (200 gm) dissolved in de-oxygenated water (600 ml), beginning cautiously and adding the last 100 ml as rapidly as possible, with vigorous stirring throughout. The ether layer containing the product was siphoned off into 500 ml conical flasks, each containing anhydrous sodium sulphate (25 gm) for drying purposes. The well-stoppered flasks could be left for several days after flushing with dinitrogen, before distillation procedures to recover the triethylphosphine were begun.

In the distillation procedure the ether was distilled off (35 - 45°) and the pale yellow crude product then transferred to a micro-distillation apparatus with an attachment for ampouling liquids under dinitrogen. The first 2 ml of distillate were

discarded and the product triethylphosphine, b.pt. 128-130°/1.013 KPa c f. lit.[46] 127°/1.013 KPa, was collected in ampoules of suitable size for use in the envisaged preparations. The ampoules were temporarily sealed with rubber sleeves and burette clips and the permanent seal was made using a coal gas/oxygen flame.

The yield was never greater than 40% (based on the amount of phosphorus trihalide used).

(ii) Organolithium Method[214,215] The reaction involved two steps; the first was the preparation of ethyllithium, and the second was the interaction of phosphorus trichloride with the ethyllithium at low temperatures. The yield of product was meagre and the reaction was not further investigated.

(b) Diethylphenylphosphine, Et_2PhP

In the initial stages of this work the above ligand was purchased from Strem Chemical Company. However upon the loan of a quantity of dichlorophenylphosphine from Dr D.A.R. Happer of this Department, an analogous preparation to that for triethylphosphine gave the required diethylphenylphosphine ligand in relatively good yield (55% in one preparation). It had a boiling point of 205°/1.013 KPa c f. lit.[216] 96-7°/0.0133 KPa, and was checked for purity by comparing the ^1H NMR spectrum with that of an authentic sample.

(c) (p-methoxyphenyl) diethylphosphine[217]

(i) (p-methoxyphenyl) dichlorophosphine. The basic procedure involved a Friedel-Crafts reaction between phosphorus trichloride and methyl phenyl ether, as follows.

Methyl phenyl ether (45gm, 0.41 mole) and anhydrous ferric chloride (30gm, 0.19 mole) were mixed together in a 1 litre, 3-necked flask fitted with a stirrer, condenser, dinitrogen inlet,

and dropping funnel. Phosphorus trichloride (57gm, 0.41 mole) was added dropwise with stirring. The reaction mixture was stirred at the boil for five hours under a steady flow of dry dinitrogen. The dense clouds of hydrogen chloride produced in the reaction were absorbed in water. The black viscous reaction mass was extracted with light petroleum (50-70, 2 x 200 ml) and the solvent distilled off. The crude product was distilled in vacuo to give (p-methoxyphenyl) dichlorophosphine, b.pt. 145°/0.02 KPa c.f. lit.[218] 140-140.5°/0.0147 KPa.

(ii) (p-methoxyphenyl) diethylphosphine. The Grignard method was used to prepare the required ligand. Preparative details are analogous to those for triethylphosphine except that the reaction was carried out at room temperature, rather than -40°.[219] The yield was 2.5 gm (24%) based on 10 gm of (p-methoxyphenyl) dichlorophosphine starting material. The (p-methoxyphenyl) diethylphosphine had b.pt. 160°/0.02 KPa c.f. lit.[220] 166-171°/0.0254 KPa. It was characterised by ^{1}H NMR (Chapter 4) and by analysis of the yellow crystalline complex formed with potassium tetrachloropalladite, dichlorobis ((p-methoxyphenyl) diethylphosphine) palladium (II). Analysis: Calculated for $C_{22}H_{34}O_2P_2Cl_2Pd$, C = 44.4%, H = 6.19%. Found: C = 45.03%; H = 5.96%.

(d) (p-dimethylaminophenyl) diethylphosphine[221]

(i) (p-dimethylaminophenyl) dichlorophosphine. As for the p-methoxy analogue the preparative method involved a Friedel-Crafts type reaction between N,N dimethylaniline and phosphorus trichloride. However because of the highly activating substituent on the aniline derivative there was no need to employ a catalyst. The procedure is as follows.

Phosphorus trichloride (69gm, 0.5 mole) and N,N

dimethylaniline (121gm, 1 mole) were placed in a 1 litre, 3-necked flask fitted with a stirrer, thermometer, reflux condenser and dinitrogen inlet. With the temperature maintained at 70° the mixture was stirred slowly for five hours. Dense clouds of hydrogen chloride were evolved and white needle crystals of N,N dimethylaniline hydrochloride formed on the sides of the flask. At the completion of the refluxing period the mixture was extracted with ether/benzene (1:1, 3 x 100 ml) and the solvents removed by distillation. The product solidified to give white low melting crystals (48gm, 43%) which were not further purified.

(ii) (p-dimethylaminophenyl) diethylphosphine. The dichlorophosphine prepared above was added at room temperature to ethylmagnesium bromide. After distillation of the ether layer followed by microdistillation of the crude product, (p-dimethyl-aminophenyl) diethylphosphine was obtained. B.pt. 158°/0.02 KPa. Yield 35gm (25%).

(e) (p-chlorophenyl) diethylphosphine[222]

The dichlorophosphine precursor of this compound was prepared by decomposing the diazonium fluoroborate salt of p-chloroaniline in the presence of phosphorus trichloride, as in the following method.

(i) p-chlorobenzenediazonium fluoroborate. p-chloroaniline (64gm, 0.5 mole) was dissolved in hydrochloric acid (6M, 250ml) by warming on a steam bath. The dark solution so formed was cooled in an ice-salt bath. White crystals of p-chloroaniline hydrochloride separated out on vigorous stirring. Diazotization was carried out by addition of sodium nitrite (36.5gm, 0.53 mole) in water (75ml) over 15 minutes with stirring. The reaction mixture temperature was maintained between 0° and 5° by addition of crushed ice as required. The resulting solution was clear black in colour. The completeness of the diazotization process was ascertained by checking

for excess of sodium nitrite with starch/potassium iodide paper.

A chilled solution of sodium fluoroborate (76gm, 0.69 mole) in water (150ml) was added slowly with vigorous stirring. The product which precipitated was filtered and washed with ice-cold water (30ml) followed by methanol (15ml) and ether (40ml) to yield white needles of p-chlorobenzenediazonium fluoroborate (84gm, 75%).

(ii) (p-chlorophenyl) dichlorophosphine. In a 1 litre, 3-necked flask equipped with a stirrer, reflux condenser, and dinitrogen inlet were reacted p-chlorobenzenediazonium fluoroborate (62.7gm, 0.30 mole), cuprous bromide (2.35gm) and phosphorus trichloride (48gm, 0.35 mole), with ethyl acetate (A.R., 250ml) as the solvent. After stirring for 30 minutes the mixture was warmed to 40°. When the vigorous reaction was complete, magnesium turnings (7.29gm, 0.30 mole) were added slowly with the temperature held between 40° and 50°. The dark brown reaction mass was distilled to remove the solvent and any unreacted phosphorus trichloride. The viscous glue-like residue was extracted with benzene/hexane solution (1:1, 3 x 100 ml) and the solvents distilled off. Vacuum distillation of the crude product gave the product, (p-chlorophenyl) dichlorophosphine, as a yellow liquid (21.7gm, 34%). b.pt. 132°/0.02 KPa.

(iii) (p-chlorophenyl) diethylphosphine. The room temperature reaction of (p-chlorophenyl) dichlorophosphine with ethylmagnesium bromide gave the crude product. This was vacuum distilled to give (p-chlorophenyl) diethylphosphine (1.2gm, 6%). b.pt. 112°/0.02 KPa c.f. lit.[222] 89-90°/0.00535 KPa. The product was contaminated by decomposition products as shown by ^{1}H NMR.

SECTION 6.2. PREPARATION OF STARTING MATERIALS

(a) Sodium (or potassium) perrhenate

Rhenium metal in powder form was treated with excess of hydrogen peroxide (130 volumes) and heated on a hot plate until dissolution was complete. The stoichiometric amount of sodium (or potassium) chloride was added and the solution concentrated to a small volume. This was heated further under an infra-red lamp to dryness and the white product was recrystallised from water. The conversion was essentially quantitative. Sodium (or potassium) hydroxide can be used in place of the appropriate halide.

(b) Sodium pertechnetate

This preparation was analogous to that above for perrhenate except that heating under reflux was necessary to achieve complete dissolution of the technetium metal. An infra-red lamp was used at all times in evaporation procedures. Again, the reaction was essentially quantitative.

(c) Potassium tetrachloropalladite (II)[223]

Bulk palladium metal (2gm) was dissolved in concentrated nitric acid (50ml) to which several drops of concentrated hydrochloric acid had been added. The presence of this small amount of chloride ion catalysed the solution process which was further assisted by heating on a steam bath for several hours. The dark brown solution was evaporated to dryness and the residue dissolved in concentrated nitric acid (20ml) and again evaporated to dryness. The resulting palladium nitrate was heated with concentrated hydrochloric acid (15 ml) for 30 minutes followed by addition of potassium chloride (3.0gm) in aqueous solution. The product, potassium tetrachloropalladite (II), separated as fine, golden brown needles on cooling in ice and these were dried in vacuo. Yield 5.8gm (95%).

The tetrabromo and tetraiodo analogues were prepared by shaking an aqueous solution of the tetrachloro salt for two hours with the appropriate potassium halide, in the molar ratio 1 : 5. They were not recovered from solution, but rather were used in situ for subsequent preparations.

(d) Potassium tetrachloroplatinite (II)[148]

Platinum foil (4.5gm) was dissolved in boiling aqua regia (3:1 hydrochloric acid/nitric acid) to form a deep red solution of chloroplatinic acid, H_2PtCl_6. Potassium hexachloroplatinate (IV) was precipitated from this solution by the addition of potassium chloride (3.5 gm) dissolved in water (20ml). The yellow powder was washed with ethanol (50%, 35ml) and ether (2 x 20ml) and air dried.

The hexachloroplatinate (IV) salt and water (70 ml) were placed in a 100 ml beaker on a steam bath. Reduction was carried out with freshly prepared sulphur dioxide solution. Not more than 1 ml of SO_2 solution was added at a time and the solution was stirred vigorously to ensure adequate mixing. Sufficient time for the disappearance of the SO_2 odour was allowed between additions. The solution became red as the reduction proceeded and smaller additions with longer time intervals between them were employed, continuing in this manner until only a trace of solid hexachloroplatinate (IV) remained. With an excess of the reducing agent sulphito complexes could form so the reduction process was stopped at this point. The solution was concentrated until the point of crystallisation and cooled in ice. The crude product was filtered off, redissolved in cold water (50 ml), and then refiltered to remove unreduced hexachloroplatinate (IV). Acetone/ether (1:1, 660ml) was added rapidly with stirring to the filtrate to precipitate the required compound, potassium tetrachloroplatinite (II), as a finely divided pink powder (7.7gm, 86%). The compound was filtered and air dried.

As for the palladium analogue, the tetrabromo and tetraiodo salts were prepared by shaking the tetrachloro compound with the appropriate potassium halide (molar ratio 1 : 5) for several hours. They were used in situ for subsequent work.

(e) Trichloronitrosylruthenium (II) hydrate[205]

Hydrated ruthenium trichloride (2gm) was dissolved in ethanol (100ml) and nitric oxide was passed through the solution for eight hours. The ethanol was evaporated from the wine red solution so formed to give a dark red amorphous mass, probably trichloronitrosylruthenium (II) pentahydrate[204]. This was used in subsequent preparations without further purification.

Nitric oxide was prepared by dropping sulphuric acid (2M) on to a stirred solution of sodium nitrite. The gas was passed through sodium hydroxide solution (10M) and through solid potassium hydroxide before use.

SECTION 6.3 EXPERIMENTAL METHODS

Ultra-violet and Visible Spectra :-

Ultra-violet and visible spectra were recorded over the range 220 - 800 nm using a Varian Techtron 635 spectrophotometer and over 220 - 1200 nm using a Shimadzu MPS 50L instrument. Solvents were chosen on the basis of the solubility of the complexes; methanol was used where possible, otherwise chloroform was employed. The solutions were contained in silica glass cells of 1 cm path length.

Molar extinction coefficients (ϵ) were determined according to the expression

$$\epsilon = A/C$$

where A is the absorbance and

C is the concentration in moles litre.$^{-1}$

Nuclear Magnetic Resonance Spectra :-

^{1}H NMR spectra were recorded on a Varian T-60 spectrometer in deuteriochloroform solutions using TMS and chloroform as internal standards. Spectra were reproducible to $\pm$ 0.05 Hz ($\sim$0.01 ppm).

Carbon -13 spectra were recorded on a Varian CFT-20 instrument using deuteriochloroform as solvent and as a field-frequency lock signal, with TMS as internal standard.

^{31}P NMR spectra were recorded either on a Varian T-60 instrument using a ^{31}P probe at 24.3 MHz, or on a JEOL C-60HL spectrometer operating at 24.3 MHz with external H_2O lock and using 8mm sample tubes.

Infra-red Spectra :-

Spectra in the $4000cm^{-1}$ - $400cm^{-1}$ region were recorded as nujol mulls on potassium bromide plates using a Shimadzu IR 27G spectrophotometer. The spectra were calibrated with polystyrene film.

Spectra in the low frequency region ($400cm^{-1}$ - $40cm^{-1}$) were recorded on an R.I.I.C. FS 720 interferometer as nujol mulls on polythene discs.

Magnetic Susceptibilities :-

Magnetic susceptibilities were determined using the Gouy method with the compound tris(ethylenediamine) nickel (II) thiosulphate as a calibrant. Gram magnetic susceptibilities (χ_g) were calculated from the formula

$$10^6 \chi_g = (\alpha - \beta F)/W$$

where W is the weight of the sample and α and β are tube constants. F is the difference in weight of the sample in

the presence or absence of a magnetic field.

Analyses :-

Carbon and hydrogen were determined at the Microanalytical Laboratory, University of Otago, Dunedin.

Melting Points :-

Melting points were determined in capilliary tubes using an Electrothermal melting point apparatus.

X-Ray Powder Photography :-

Powder photographs were taken with Philips Debye-Scherrer powder cameras of internal diameter 57.3 mm, using Cu Kα radiation. Exposure times for chloro and bromo complexes were of approximately four hours duration but at least twelve hours were required for iodo complexes.

Purification of Solvents :-

Benzene

The solvent was heated under reflux over phosphorus pentoxide for several hours and then distilled off and stored over molecular sieves.

Ether

The solvent was dried with sodium wire.

Tetrahydrofuran

THF was heated under reflux over sodium hydride for three hours and stored over molecular sieves.

Dimethylformamide

The solvent was stored over potassium hydroxide pellets.

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